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Polyvinyl Chloride

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16. ABSTRACT

This report summarizes data on air emissions from the polyvinyl chloride (PVC) industry. PVC is manufactured by 20 companies at 35 plants. Each plant uses one or more of four possible polymerization processes: (1) suspension polymerization, (2) emulsion polymerization, (3) bulk polymerization, and (4) solution polymerization. A representative PVC plant was defined to assess the severity of emissions from this industry. Source severity, defined as the ratio of the time-averaged maximum ground level concentration of a pollutant to a hazard potential, was calculated for 16 chemical species emitted from a representative plant. The two largest severities were 970 for vinyl chloride and 1.9 for PVC. Control technology for hydrocarbons includes adsorption, absorption, refrigeration, incineration, stripping, purging of equipment with inert gas or water, and control of fugitive emissions.

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POLYVINYL CHLORIDE

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains an assessment of air emissions from the production of polyvinyl chloride. This study was conducted to provide an overview of the information available on polyvinyl chloride plants, including process technology, industry structure, control technology, and ambient concentrations. Further information on this subject may be obtained from the Organic Chemicals and Products Branch, Industrial Pollution Control Division.

David G. Stephan
Director
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PREFACE

The Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA) has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act, and solid waste legislation. If control technology is unavailable, inadequate, or uneconomical, then financial support is provided for the development of the needed control techniques for chemical and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

IERL has the responsibility for developing control technology for a large number of operations (more than 500) in the chemical and related industries. As in any technical program, the first step is to identify the unsolved problems. Each of the industries is to be examined in detail to determine if there is sufficient potential environmental risk to justify the development of control technology by IERL. This report provides an overview of the information available on polyvinyl chloride plants, including process technology, industry structure, control technology, and ambient concentrations.

Monsanto Research Corporation (MRC) has contracted with EPA to investigate the environmental impact of various industries that represent sources of emissions in accordance with EPA's responsibility, as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program, entitled "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer for this series. This study of polyvinyl chloride plants was initiated by IERL-Research Triangle Park in March 1975; Mr. Kenneth Baker served as EPA Project Leader. The project was transferred to the Industrial Pollution Control Division, IERL-Cincinnati in October 1975; Mr. Ronald J. Turner served as EPA Project Leader from that time through completion of the study.

ABSTRACT

This report describes a study of air emissions from polyvinyl chloride production. The study was completed to provide EPA with sufficient information to determine whether additional control technology needs to be developed for this emission source.

Polymers derived from vinyl chloride monomer (VCM) are called polyvinyl chloride (PVC). The 1974 consumption of PVC was 2.2×10^6 metric tons/yr which represented the third largest volume of plastic consumed. PVC is manufactured by 20 companies at 35 plants. Each plant uses one or more of four possible polymerization processes: 1) suspension polymerization, 2) emulsion polymerization, 3) bulk polymerization, and 4) solution polymerization, which account for 78%, 13%, 6% and 3% of the total production capacity, respectively.

A representative PVC plant is defined as one using the suspension process and having a nominal production capacity of 68×10^3 metric tons, a population density surrounding the plant of 313 persons/km^2, average emission heights for vinyl chloride monomer and polyvinyl chloride resin dust (particulates) of 15.5 m and 21 m, respectively. The emission factors for vinyl chloride and polyvinyl chloride from the representative plant are 35.5 g/kg and 7.5 g/kg, respectively.

To assess the potential environmental effect of emissions from this industry, the source severity (defined as the ratio of the time-averaged maximum ground level concentration of a pollutant to a hazard potential) was calculated for 16 chemical species emitted from the representative plant. The two largest source severities were for vinyl chloride (970) and polyvinyl chloride (1.9).

Polyvinyl chloride production in 1974 amounted to 2.22×10^6 metric tons and is expected to grow at a rate of 5.2%/yr through 1978 when production is estimated to be 2.86×10^6 metric tons. If the 1978 level of emissions control is the same as the 1973 level, emissions from PVC manufacture will increase by 29% over that period.

This report was submitted in partial fulfillment of Contract No. 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period March 1975 to July 1977, and work was completed as of August 1977.

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ABBREVIATIONS AND SYMBOLS

A	-- affected area
A_R	-- factor defined as $Q/ac\pi u$
AAQS	-- ambient air quality standard
a,..f,v..z	-- constants
B_R	-- factor defined as $-H^2/2c^2$
C_i	-- production capacity of plant i
$\bar{D}_P$	-- capacity-weighted mean population density
$\bar{D}_{P_i}$	-- county population density for plant i
e	-- constant; 2.72
exp	-- natural log base, e
F	-- hazard factor; for criteria pollutants, F is the primary ambient air quality standard; for noncriteria pollutants, F is a reduced TLV value
H	-- effective emission height
P	-- total affected population
PVC	-- polyvinyl chloride
Q	-- mass emission rate
S	-- source severity
S_{HC}	-- source severity for hydrocarbon emissions
S_P	-- source severity for particulate emissions
S_{VCM}	-- source severity for vinyl chloride
t	-- averaging time for ambient air quality standard
t_o	-- "instantaneous" averaging time
TLV	-- threshold limit value
u	-- wind speed
$\bar{u}$	-- average wind speed
VCM	-- vinyl chloride monomer
x	-- downwind distance from source of emission
x_1, x_2	-- roots of equation for affected area calculation

ABBREVIATIONS AND SYMBOLS (continued)

y	-- horizontal distance from centerline of dispersion
z	-- vertical distance from centerline of dispersion
π	-- constant; 3.14
σ_y	-- standard deviation of horizontal dispersion
σ_z	-- standard deviation of vertical dispersion
χ	-- downwind ground level concentration of a pollutant
$\bar{\chi}$	-- average downwind ground level concentration of a pollutant
χ_{max}	-- maximum ground level concentration of a pollutant
$\bar{\chi}_{max}$	-- time-averaged maximum ground level concentration of a pollutant
$\bar{\chi}(x)$	-- annual mean ground level concentration of a pollutant at a specific distance (x) from the source

CONVERSION FACTORS AND METRIC PREFIXES[a]

CONVERSION FACTORS

To convert from	to	Multiply by
Degree Celsius (°C)	Degree Fahrenheit	$t° = 1.8\ t° + 32$
Grams/second (g/s)	Pounds/hr	7.936
Joule (J)	Calorie	2.388×10^{-1}
Kilogram (kg)	Pound-mass (avoirdupois)	2.204
Kilogram/meter^3 (kg/m^3)	Pound/foot^3	6.243×10^{-2}
Kilometer^2 (km^2)	Mile^2	3.860×10^{-1}
Meter (m)	Foot	3.281
Meter^3 (m^3)	Feet^3	3.531×10^{1}
Metric ton	Kilogram	1.000×10^{3}
Metric ton	Pound-mass	2.205×10^{3}
Metric ton	Ton (short, 2,000 pound mass)	1.102
Pascal (Pa)	Atmosphere	9.869×10^{-6}
Pascal (Pa)	Torr (mm Hg, 0°C)	7.501×10^{-3}
Pascal (Pa)	Pound-force/inch (psi)	1.450×10^{-4}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Kilo	k	10^3	1 kPa = 1×10^3 pascals
Mega	M	10^6	1 MJ = 1×10^6 joules
Micro	μ	10^{-6}	1 g = 1×10^{-6} gram

SECTION 1

INTRODUCTION

Products and components fabricated from polyvinyl chloride are used in nearly every branch of industrial and commercial activity -- building and construction, home furnishings, consumer goods, electrical devices and goods, packaging, and transportation.

Polyvinyl chloride resins are manufactured by four polymerization processes: suspension polymerization (the largest production method), emulsion polymerization, bulk polymerization, and solution polymerization.

This document assesses the atmospheric emissions and potential environmental effects of polyvinyl chloride polymerization processes, using data determined from literature references.

The major findings of this study are summarized in Section 2. Section 3 provides detailed descriptions of the polyvinyl chloride polymerization processes, including the major processing steps, flow diagrams, process chemistry, and material and energy balances.

Section 4 discusses types of emissions, emission points, mass of emissions, ground level concentrations, source severity and affected population.

Section 5 considers the present and future aspects of pollution control technology in the polyvinyl chloride industry. The growth and nature of the industry are discussed in Section 6.

SECTION 2

SUMMARY

Polymers derived from vinyl chloride monomer (VCM) are called polyvinyl chloride (PVC). These polymers may be homopolymers, which are made only from vinyl chloride monomer, or copolymers, made from vinyl chloride monomer and another monomer such as vinyl acetate, ethylene, propylene, vinylidene chloride, or an acrylate. Polyvinyl chloride is used in the manufacture of apparel, building and construction materials, wire and cable insulation, home furnishings, packaging, recreation items, transportation components, and other saleable commodities. The 1974 consumption of polyvinyl chloride was 2.2×10^6 metric tons/yr;[a] it was the third largest volume plastic, trailing only low density polyethylene and styrenics in consumption.

PVC is manufactured by 20 companies at 35 plants. With individual production capacities ranging from 6.8×10^3 metric tons/yr to 136×10^3 metric tons/yr, these plants have a combined capacity of 2.4×10^6 metric tons/yr. Each of the plants uses one or more of four possible polymerization processes: 1) suspension polymerization, 2) emulsion polymerization, 3) bulk polymerization, and 4) solution polymerization, which account for 78%, 13%, 6% and 3% of the total production capacity, respectively. PVC production causes atmospheric emissions consisting of criteria pollutants and chemical substances. Criteria pollutants include hydrocarbons (volatile organic materials), sulfur oxides (SO_x), and particulates (airborne polyvinyl chloride resin dust). Chemical substances include vinyl chloride, ethylene, propylene, acetylene, butadiene, ethylene dichloride, vinylacetate, vinyl bromide, vinylidene chloride, acetaldehyde, ethyl chloride, chloroprene, hydrogen chloride, and phenol. Table 1 lists emission factors for atmospheric emissions from a representative polyvinyl chloride plant using the suspension process. These materials are emitted inside each plant from reactor safety relief valves, reactor entry purges, stripper jets, monomer recovery condenser vents, slurry blend tank vents, centrifuge vents, dryer discharges, resin storage silos, bulk loading facilities, bagger vents, storage tanks, and fugitive emission points. In a typical PVC plant, there may be 600 or more separate emission points.

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[a] 1 metric ton = 10^6 grams = 2,205 pounds; conversion factors and metric system prefixes are presented in the prefatory pages.

TABLE 1. EMISSION FACTORS FOR A REPRESENTATIVE POLYVINYL CHLORIDE PLANT (SUSPENSION PROCESS)

Material emitted	Emission factor, g/kg
Vinyl chloride	35.5 ± 8.24[a]
Polyvinyl chloride	7.5 ± 3.18[a]
Stabilizer (phenol)	204×10^{-5}
Ethyl chloride	92×10^{-5}
Sulfur oxides	23×10^{-5}
Butadiene	21×10^{-5}
Hydrogen chloride	21×10^{-5}
Vinylidene chloride	9×10^{-5}
Acetaldehyde	7×10^{-5}
Acetylene	7×10^{-5}
Propylene	7×10^{-5}
Vinylacetylene	5×10^{-5}
Ethylene	5×10^{-5}
Ethylene dichloride	4×10^{-5}
Chloroprene	$<4 \times 10^{-5}$
Vinyl bromide	2×10^{-5}

[a]These values indicate the mean values for the emission factor; the 95% confidence limit is given in g/kg.

Atmospheric emissions from a representative PVC plant have been determined and are presented in this document. A representative PVC plant was defined as one using the suspension process and having the following mean values for various plant parameters:

- Nominal production capacity of 68×10^3 metric tons.
- Population density surrounding the plant of 313 persons/km^2.
- Average emission height for vinyl chloride monomer of 15.5 m.
- Average emission height for polyvinyl chloride resin dust (particulates) of 21 m.
- Total vinyl chloride emission factor of 35.5 g/kg.
- Total polyvinyl chloride emission factor of 7.5 g/kg.

The representative plant (defined on page 39) is typical of 78% of the total production capacity of PVC in the United States. The remaining 22% of production capacity consists of polyvinyl chloride produced via the emulsion, bulk, and solution polymerization process; these have vinyl chloride emission factors of 60.1 g/kg, 24.2 g/kg, and 17.8 g/kg, respectively.

Atmospheric emissions from the representative source have been characterized in this assessment by calculation of a source severity, determination of the national burden of criteria pollutants, determination of state burdens of criteria pollutants, estimation of the population affected by the atmospheric emissions, and estimation of the rate of increase of emission with time.

Source severity is defined as the time-averaged maximum ground level concentration divided by a hazard potential. The time-averaged maximum ground level concentration is determined using Gaussian plume dispersion methodology. The hazard potential is equal to the primary ambient air quality standard for criteria pollutants and to a reduced threshold limit value (TLV®) for chemical substances. Table 2 lists source severities and TLV's for atmospheric emissions from a representative polyvinyl chloride plant.

TABLE 2. SOURCE SEVERITY BY COMPOUND FOR A REPRESENTATIVE POLYVINYL CHLORIDE PLANT

Material emitted	TLV, g/m^3	Source severity[a]
Vinyl chloride	0.0026	970
Polyvinyl chloride	0.1090	1.9
Stabilizer (phenol)	0.02	7.2×10^{-3}
Ethyl chloride	2.60	2.5×10^{-5}
Sulfur oxides	0.013	1.3×10^{-3}
Butadiene	2.20	6.8×10^{-6}
Hydrogen chloride	0.007	2.1×10^{-3}
Vinylidene chloride	0.004	1.6×10^{-3}
Acetaldehyde	0.18	2.8×10^{-5}
Acetylene	1.16	4.3×10^{-6}
Propylene	1.88	2.6×10^{-6}
Vinylacetylene	0.048	7.4×10^{-5}
Ethylene	1.25	2.8×10^{-6}
Ethylene dichloride	0.20	1.4×10^{-5}
Chloroprene	0.09	3.2×10^{-5}
Vinyl bromide	1.10	1.3×10^{-6}

[a] $\text{Source severity} = \dfrac{\bar{\chi}_{max}}{\text{TLV} \times 8/24 \times 1/100}$

The national mass of criteria pollutants emitted from PVC plants and their percent contributions to national emissions are shown in Table 3.

TABLE 3. POLYVINYL CHLORIDE INDUSTRY CONTRIBUTIONS TO NATIONAL STATIONARY SOURCE EMISSIONS OF CRITERIA POLLUTANTS

Material emitted	Total national emission (1), 10^6 metric tons/yr	Emissions from the PVC industry, 10^3 metric tons/yr	Emissions from the PVC industry, Percent of national emissions
Hydrocarbons (vinyl chloride, phenol stabilizer, ethyl chloride, butadiene, vinylidene chloride, acetaldehyde, acetylene, propylene, vinylacetylene, ethylene, ethylene dichloride, chloroprene, vinyl bromide)	25	85	0.34
Particulate (polyvinyl chloride)	18	18	0.10
Sulfur oxides	30	5.5×10^{-4}	2×10^{-6}

Hydrocarbon emissions from PVC plants in New Jersey, Massachusetts, West Virginia, Delaware, Kentucky, Oklahoma, and Mississippi range from 1.1% to 6.9% of each state's hydrocarbon emissions. New Jersey has particulate emissions from PVC plants which represent 1.6% of the state's total particulate emissions. All other states with PVC plants have hydrocarbon and particulate emissions from polyvinyl chloride manufacture which are less than 1% of the state totals. Table 4 gives a complete list of polyvinyl chloride industry contributions to state emissions of criteria pollutants.

PVC plants are located in counties with population densities ranging from 9 to 1,900 persons/km^2, with the population for the representative source being 313 persons/km^2. The area surrounding the representative plant for which the source severity for vinyl chloride monomer is greater than or equal to 0.1 was calculated to be 2,780 km^2. The affected population is thus 870,000 persons for the representative source.

Polyvinyl chloride production in 1973 amounted to 2.22×10^6 metric tons and is expected to grow at a rate of 5.2%/yr through 1978 when production is estimated to be 2.86×10^6 metric tons. If the 1978 level of emissions control is the same as the 1973 level, emissions from PVC manufacture will increase by 29% over that period.

(1) 1972 National Emissions Report. EPA-450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 422 pp.

TABLE 4. POLYVINYL CHLORIDE INDUSTRY CONTRIBUTIONS TO STATE EMISSIONS OF CRITERIA POLLUTANTS (1)

State	Material emitted[a]	State emissions, 10^3 metric tons/yr	PVC emissions	
			metric tons/yr	Percent
New Jersey	Vinyl chloride	819.5	9,450	1.15
	PVC	151.8	2,370	1.56
Massachusetts	Vinyl chloride	440.5	5,845	1.33
	PVC	96.16	855	0.09
Ohio	Vinyl chloride	1,153	10,620	0.92
	PVC	1,766	3,030	0.17
California	Vinyl chloride	2,161	2,145	0.10
	PVC	1,006	1,505	0.15
West Virginia	Vinyl chloride	116.2	8,030	6.91
	PVC	213.7	380	0.18
Illinois	Vinyl chloride	1,826	7,090	0.39
	PVC	1,143	1,775	0.16
Texas	Vinyl chloride	2,219	6,980	0.31
	PVC	549.4	1,820	0.33
Delaware	Vinyl chloride	63.89	2,770	4.34
	PVC	36.81	2,870	0.78
Louisiana	Vinyl chloride	1,920	6,915	0.36
	PVC	380.6	715	0.19
New York	Vinyl chloride	1,262	2,055	0.16
	PVC	160	150	0.09
Kentucky	Vinyl chloride	326.3	7,380	2.26
	PVC	546.2	1,295	0.24
Florida	Vinyl chloride	619.9	1,075	0.17
	PVC	226.5	490	0.22
Maryland	Vinyl chloride	295.9	1,860	0.63
	PVC	494.9	510	0.10
Oklahoma	Vinyl chloride	341.4	3,660	1.07
	PVC	93.6	65	0.07
Mississippi	Vinyl chloride	196	4,185	2.14
	PVC	168.4	885	0.52
Pennsylvania	Vinyl chloride	891.8	4,150	0.47
	PVC	1,811	365	0.02

[a]Vinyl chloride hydrocarbon emission; PVC particulate emission.

Available emissions control technology is divided into hydrocarbon control and particulate control. Controls for hydrocarbons include adsorption, absorption, refrigeration, incineration, stripping, purging of equipment with inert gas or water, and control of fugitive emissions.

Fugitive emissions are being reduced through the use of a monitoring program. Double mechanical seals and leakproof metal discs are used to control fugitive emissions from leaking pumps,

compressors, agitators, seals, and pressure relief valves. Process modifications to control fugitive emissions include the use of larger reactors in newer plants. Since large reactors require fewer connections, they reduce fugitive emissions by reducing the number of potential leaks. EPA standards on vinyl chloride emissions require a 95% or better reduction in atmospheric vinyl chloride emissions.

Particulate emissions are being controlled through the use of fabric filters and cyclonic collectors.

When the link between VCM and cancer was established in 1974, the PVC industry entered a new era. The emission and control data used in this report were obtained in 1974 before the recent dynamic changes in the industry. Many plants currently report meeting emission standards established by EPA and OSHA.

SECTION 3

SOURCE DESCRIPTION

Polyvinyl chloride is one of the three largest volume thermoplastics produced in the United States (2). In 1974 there were 20 companies at 35 locations in the United States (3) capable of producing 2.45×10^6 metric tons/yr of PVC. PVC is produced by VCM polymerization in one of four processes. Three of these are batch processes - suspension polymerization (which accounts for 78% of capacity); emulsion polymerization (13%); and bulk polymerization (6%). The fourth process, solution polymerization, is a continuous process and accounts for 3% of the PVC resin capacity (4).

The suspension process for manufacturing PVC is described in detail below. The other three processes are briefly described in terms of their variations from the suspension process.

PROCESS DESCRIPTION

Suspension Polymerization

The suspension process accounts for 78% of the polyvinyl chloride homopolymers and copolymers made in the United States (5).

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(2) Olivier, G. What's the Future for PVC? Hydrocarbon Processing, 45(9):281-284, 1966.

(3) PVC Chemical Profile. Chemical Marketing Reporter. 205(20):9, 1974.

(4) Evans, L., C. Kleeberg, S. Wyatt, A. Basola, W. Hamilton and W. Vatavuk. Standard Support - Environmental Impact Document. An Investigation of Health Effects and Emission Reduction of Vinyl Chloride in the Vinyl Chloride Monomer and Polyvinyl Chloride Industries. Volume II. Draft copy of report. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1975. 450 pp.

(5) Carpenter, B. H. Vinyl Chloride - An Assessment of Emissions Control Techniques and Costs. EPA-650/2-74-097, U.S. Environmental Protection Agency, Washington, D.C., September 1974. 84 pp.

Suspension polymerization is applied to a system in which the water-insoluble monomer is suspended as liquid droplets, and the resultant polymer is obtained as a dispersed solid phase. Initiators used in the process are soluble in the liquid monomer phase (6).

Figure 1 depicts dispersed vinyl chloride droplets suspended in a water medium. Mechanical agitation causes the larger unstable droplets to break into smaller ones. The smaller droplets coalesce and reform into larger droplets until a dynamic equilibrium between dispersion and coalescence is reached (7).

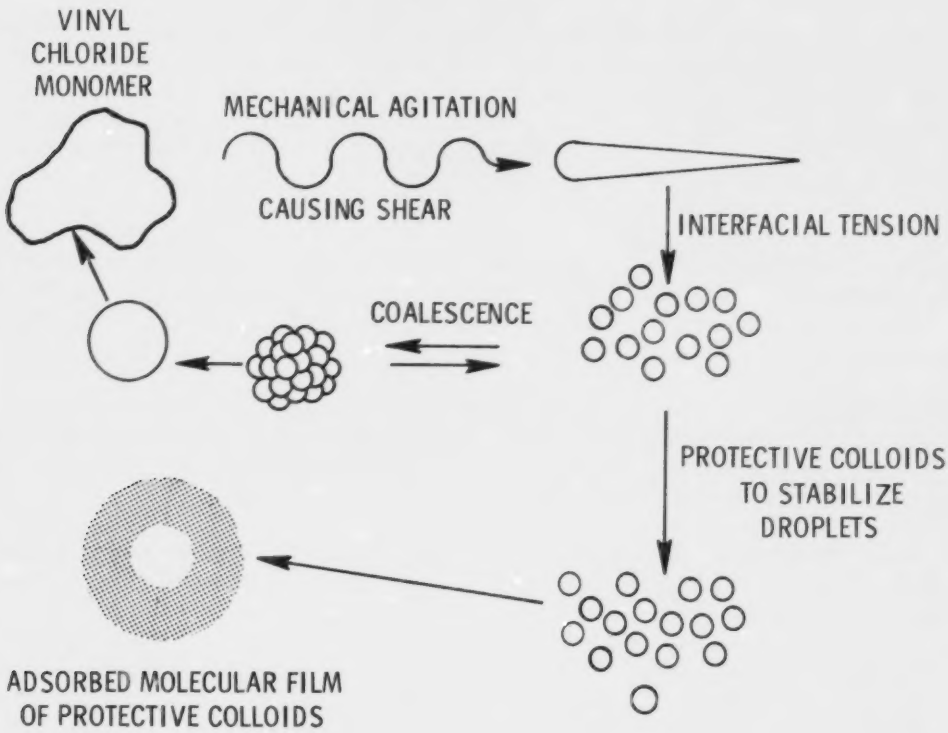

Figure 1. Suspension polymerization.

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(6) Suspension Polymerization. In: Encyclopedia of Polymer Science and Technology; Volume 13: Plastics, Resins, Rubber, Fibers. John Wiley & Sons, Inc., New York, New York, 1970. pp. 552-571.

(7) Albright, L. F. Polymerization of Vinyl Chloride. Chemical Engineering, 74(10):151-158, 1967.

Protective colloids, which are water-soluble, are added to stabilize the vinyl chloride droplets and help prevent agglomeration of PVC droplets. Colloids increase the viscosity of the water layer and delay coalescence (7).

A water-soluble initiator starts the polymerization process. As polymerization occurs, the viscosity of the organic phase increases, and polymer molecules form throughout the droplets (7). PVC produced in the dispersed vinyl chloride droplets forms a solid phase, since polyvinyl chloride is insoluble in vinyl chloride (7). At this stage, the reduction in vinyl chloride concentration is accompanied by an increase in the polymerization rate instead of the expected decrease. Autoacceleration of the reacting medium (7) explains this phenomenon.

Polymerization occurs in both the VCM and PVC phases. In the PVC phase, VCM diffuses to the active sites located throughout the semisolid PVC phase, and polymerization occurs. Due to limited mobility in the PVC phase, these active sites cannot react with each other to cause coupling or disproportionation reactions that destroy free radicals (7).

Figure 2 is a block flow diagram (8); Figures 3a and 3b are detailed flowsheets (4, 5, 8-12) of the manufacture of PVC by the suspension process. Figures 3a and 3b designate representative plant emission points which are described later in Table 8 in Section 4.

Raw Materials--
The raw materials required for the suspension polymerization of vinyl chloride include vinyl chloride monomer, initiator, suspending agent, emulsifier, and deionized water.

There are numerous patents for suspension polymerization recipes (formulation) available in the literature. The basic formulation is shown in Table 5.

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(8) Kardos, L. A. Polyvinyl Chloride. Report No. 13 (a private report by the Process Economics Program), Stanford Research Institute, Menlo Park, California, June 1966. 224 pp.

(9) Labine, R. A. Drying Tricks Tailor Resin Properties. Chemical Engineering, 66(23):166-169, 1959.

(10) From Vinyl Chloride to...PVC by Suspension Polymerization. Chemical Engineering, 62(7):128, 130, 132, 1955.

(11) Ohta, K. Polyvinyl Chloride - Supplement-A. Report No. 13A (a private report by the Process Economics Program), Stanford Research Institute, Menlo Park, California, May 1970. 170 pp.

(12) Albright, L. F. Vinyl Chloride Polymerization by Suspension Process Yields Polyvinyl Chloride Resins. Chemical Engineering, 74(12):145-152, 1967.

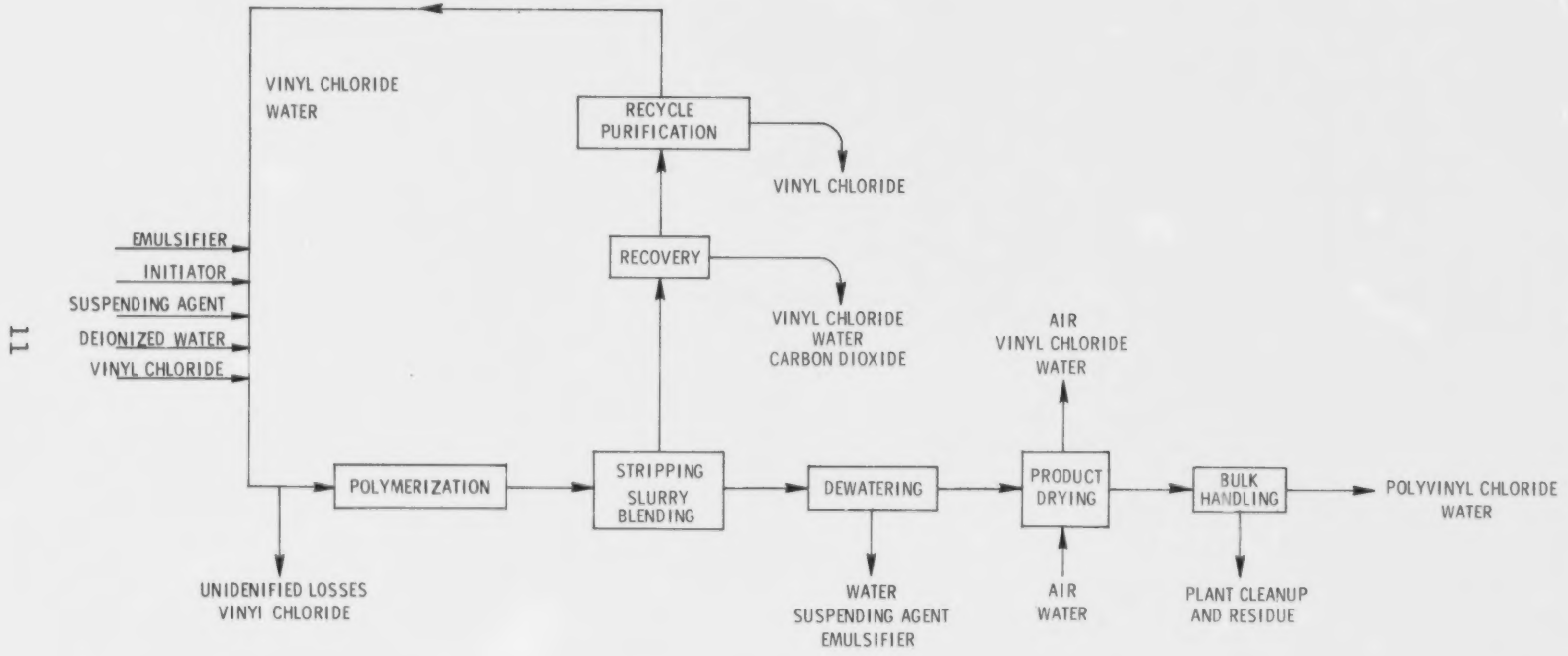

Figure 2. Block flow diagram for production of polyvinyl chloride by the suspension process.

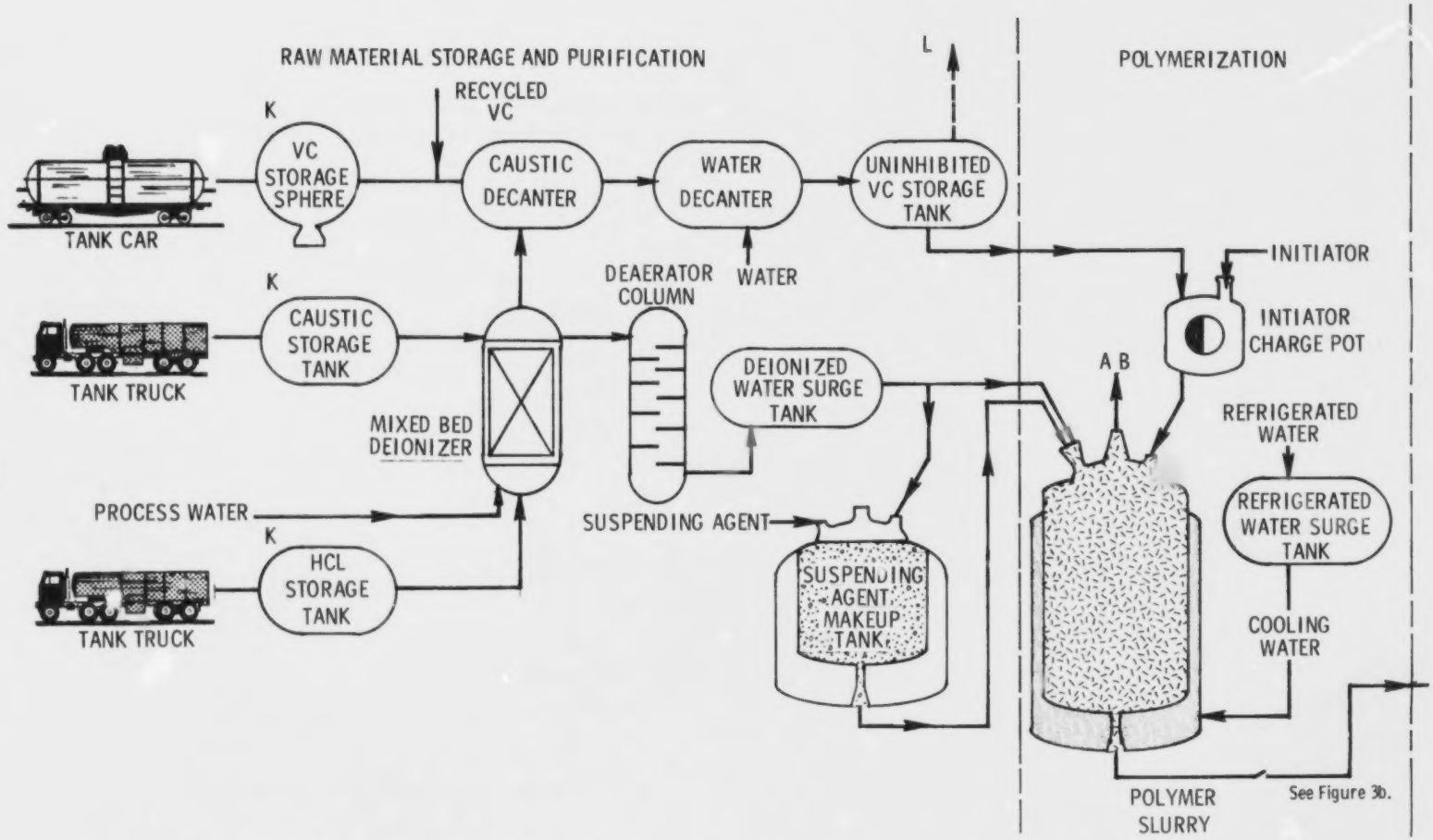

Figure 3a. Flowsheet for production of polyvinyl chloride by the suspension process.

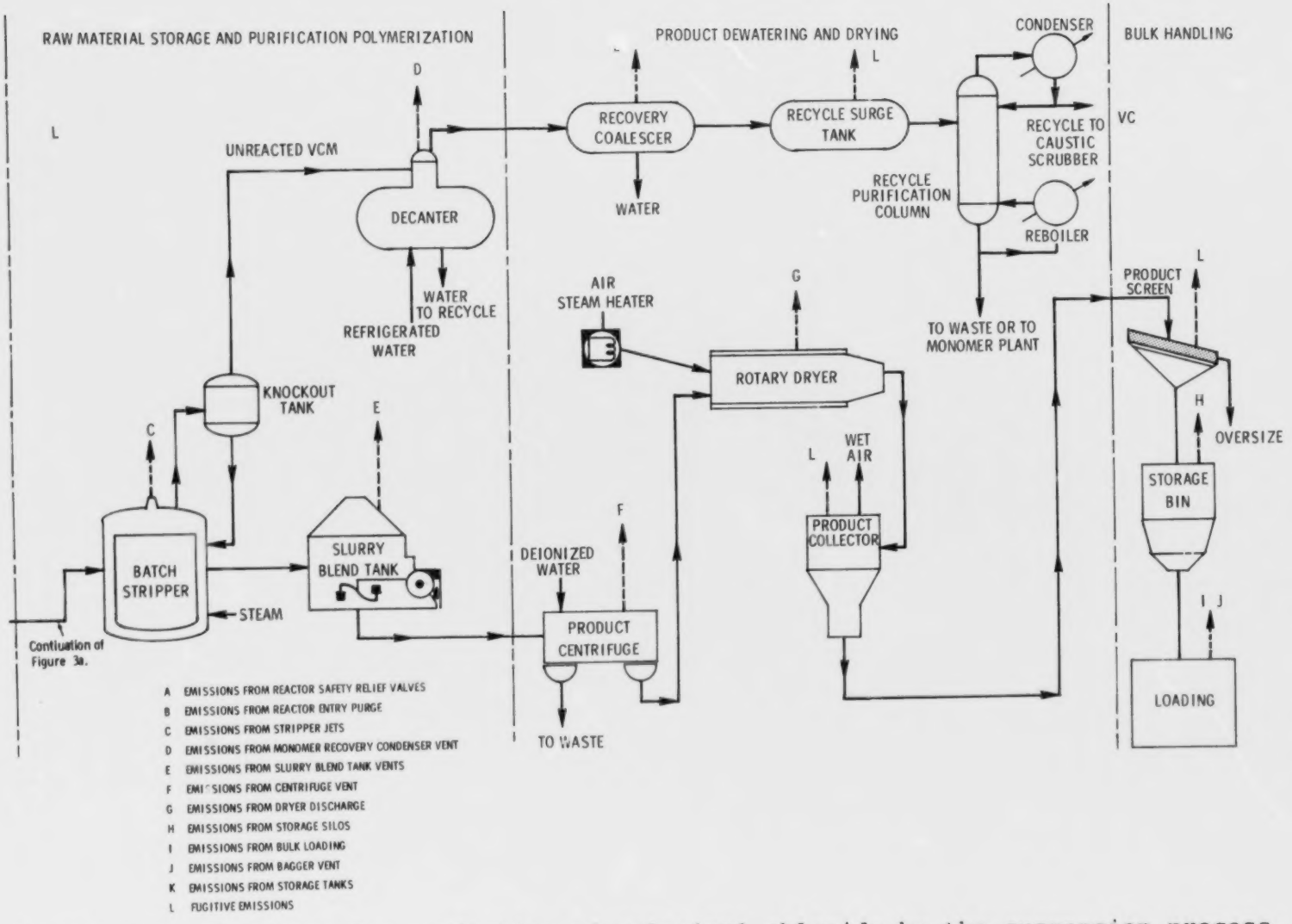

Figure 3b. Flowsheet for production of polyvinyl chloride by the suspension process.

TABLE 5. RAW MATERIALS FOR SUSPENSION POLYMERIZATION OF VINYL CHLORIDE (8)

Component	Parts by weight
Vinyl chloride monomer	100
Deionized water	200
Initiator	0.025
Suspending agent	0.04
Emulsifier	0.02

Vinyl chloride monomer--Pure monomer is used in polymerizing vinyl chloride by suspension polymerization. Specifications for commercial VCM along with the major impurities present are listed in Table 6 (9, 13, 14).

Shipping of uninhibited monomer is permitted in the United States. Some VCM is delivered to the PVC plant containing 100 ppm phenol which is used to prevent polymerization during shipment. This inhibitor must be removed by scrubbing with aqueous sodium hydroxide (9).

TABLE 6. VINYL CHLORIDE MONOMER COMPOSITION

Material	Maximum level, ppm
Vinyl chloride	<99.9%
Ethylene	1.3
Propylene	2.0
Acetylene	2.0
Butadiene	6.0
Ethylene dichloride	0.1 to 2
Vinylacetylene	0.01 to 3.0
Vinyl bromide	0.05 to 1
Vinylidene chloride	0.1 to 5
Acetaldehyde	2.0
Ethyl chloride	2.0 to 50
Chloroprene	<1.0
Hydrogen chloride	2.0 to 10.0
Iron	0.4
Sulfur	3.0 to 10
Water	15.0 to 200
Nonvolatiles	10 to 200
Stabilizer (phenol)	25 to 90

(13) Lunde, K. E. Vinyl Chloride. Report No. 5 (a private report by the Process Economics Program), Stanford Research Institute, Menlo Park, California, 1965. 212 pp.

(14) Matheson Gas Data Book, Fourth Edition. The Matheson Company, Inc., East Rutherford, New Jersey, 1966. pp. 489-492.

Deionized water--Water used for suspension polymerization is deionized, deaerated, and free of organic matter and sulfur (10, 15, 16). Water serves three purposes; it provides heat transfer, it is a medium for the suspending agent which controls the surface properties of the particles and it also moderates the bulk viscosity during processing (17).

Initiators--Initiators are compounds capable of forming free radicals by thermal decomposition (8). Patent literature reports the use of many initiators. Suspension polymerization of vinyl chloride monomer is initiated by organic peroxides in industrial practice, although azo compounds, boron derivatives, and redox systems can be used (8).

Major producers report using isopropyl peroxide carbonate (IPP) (11). Figure 4 shows conversion of VCM as a function of reaction time for polymerization of vinyl chloride using two different initiators (18). Advantages claimed for the use of IPP initiator include: 1) reduced batch time; 2) little or no induction period; 3) improved polymer quality because of fewer initiator fragments; and 4) less chain branching during polymerization.

Suspending agents--Suspending agents are surface active compounds that prevent agglomeration of PVC particles during polymerization of vinyl chloride (2, 17). The suspending agent influences particle size, porosity, and thus processing characteristics of the product.

Conventional suspending systems such as natural gums and gelatin, or synthetic polymers such as partially hydrolyzed polyvinyl acetate (polyvinyl alcohol - polyvinyl acetate) and methyl cellulose, efficiently promote transition from a monomer droplet containing precipitated PVC to a polymer particle swollen with monomer (17). However, these systems produce a resin that does not readily absorb plasticizers, requiring high processing

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(15) Ruebensaal, C. F. Vinyl Resins - How Vinyl Chloride is made...How Vinyl Chloride is Polymerized. Chemical Engineering, 57(12):102-105, 1950.

(16) Meinhold, T. F., and W. M. Smith. Produces Dust Free PVC Resins. Chemical Processing, 22(7):61-62, 1959.

(17) Manufacture of Plastics, Volume I. Chapter 7. Reinhold Publishing Corporation. W. M. Smith, ed. New York, New York, 1964. pp. 303-343.

(18) Marous, L. F., and C. D. McCleary. Polymerization Catalyst for Vinyl Chloride. U.S. Patent 3,022,282 (to United States Rubber Company), February 20, 1962.

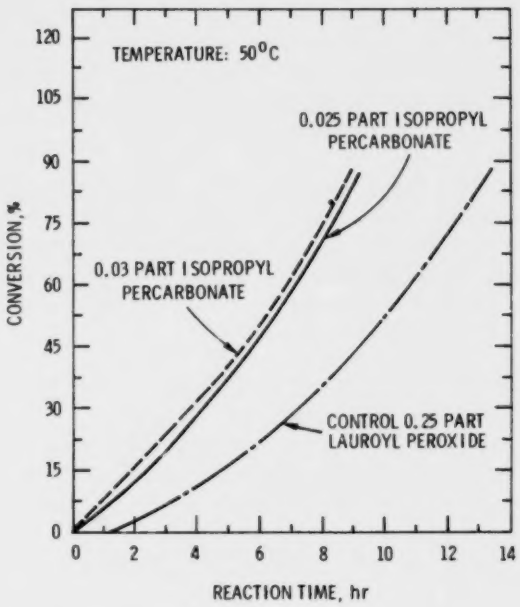

Figure 4. Effect of initiator on reaction rate during production of PVC by suspension polymerization.

temperatures or premastication in an intensive mixer or extruder before the final processing to plastic products (11).

Industry is presently investigating all synthetic suspending systems that produce "easy processing" or "fast blending" resins. These resins have high plasticizer absorption capacity in dry blending and greater ease of homogenization when subjected to heat and mechanical shear of extrusion or calendering (17).

Emulsifier--Processing of the final product is improved by the addition of small quantities of a secondary emulsifier to the system (17). Such emulsifiers include sulfonated oils or esters, ethylene oxide condensation products with polyols, and other synthetic surfactants.

Raw material storage and purification--Vinyl chloride monomer received at the plant contains phenol stabilizer to prevent polymerization during shipping. The stabilizer is removed from the monomer by caustic washing or by distilling the monomer from an aqueous caustic mixture (15,17). Heavy impurities are removed by distillation in a plate column, and the liquid monomer is stored in a refrigerated stainless steel or glass lined tank at less than 16°C and 345 kPa to retard hydrolysis and peroxide formation (17).

Water is deionized in a mixed-bed ion exchanger and then deaerated by heat and vacuum in the deareator column before use in the process (10,15,16).

The suspending agent and emulsifier are dissolved in the suspending agent solution makeup tank using deionized water. Separate charge pots and storage tanks are used to mix and proportion the initiator, hydrochloric acid, and caustic (8).

Polymerization--
Vinyl chloride polymerization is carried out in stainless steel, glass-lined carbon steel, or glass-lined stainless steel reactors, depending on raw materials used, corrosion resistance, and desired lifetime of reactors (6). Reactor sizes vary between 11.3 m^3 and 103.2 m^3; each plant uses 4 to 18 such reactors (4). Newer plants tend to have larger and fewer reactors (4). Each reactor is equipped with an agitator, baffles, and temperature controls (18).

The reactor is charged first with deionized, deaerated water; then the suspending agent solution is introduced. The temperature of the reactor is raised to 55°C by passing steam through the reactor jacket. The initiator is placed in the charge pot and dissolved by the liquid monomer as it is fed through the batch meter (8).

Cooling water is circulated through the reactor jacket to keep the temperature at 55°C during the polymerization (8).

An agitator located at the bottom of the vessel uses multiple baffles and/or multiblade shafts to provide uniform agitation (17), which is important for both efficient heat transfer and control of polymer particle size (6, 17).

Reaction temperature is one of the primary control variables in suspension polymerization (6). Temperature influences molecular weight, molecular weight distribution, crystallicity of the product, the particle size of the polymer and the solubility and adsorptivity of the suspending agent (6). A master-slave cascade instrument system is used for temperature control. Steam, cold water, and refrigerated water or brine are circulated through the reactor jacket as required. The polymerization temperature can be controlled with 30°C cooling water up to 70% conversion. Subsequently, the reaction rate increases more rapidly due to autoacceleration. At this point, refrigerated water at 16°C is required to control the temperature (8).

Polymerization takes place at a pressure of 517 kPa to 690 kPa (6). Reactors are protected from overpressure by safety relief valves and rupture discs. Completion of the reaction is indicated by a drop in pressure. Prolongation of the cycle is harmful to resin porosity and color (7). The cycle is terminated at 88% conversion (276 kPa) by blowing the slurry to the batch strippers (8).

Unreacted VCM is sent by vacuum to the recovery system and recycled. Noncondensable gases accumulate in the recovery system and must be vented.

Monomer Recovery and Slurry Blending--
In many plants, slurry from the reactor is transferred to a stripper for removal of unreacted vinyl chloride by the application of heat and/or vacuum. Stripping can also be completed effectively in the reactor, but most producers do not use reactors for the time-consuming stripping operation. Vent gas from the stripper is transferred to the vapor recovery system for recycling (4).

The monomer-free polymer slurry is transferred to the slurry blend tank, where various batches are blended together to form a uniform product. Slurry blending tanks also serve as a buffer volume between the batch polymerization in the reactor and the continuously operated equipment downstream (8). These tanks are open and release residual VCM to the atmosphere.

Polymer Dewatering and Drying--
Slurry from the blend tank is pumped to a centrifuge for separation of the polymer and water. The centrifuge is conical; the bowl rotates at 500 rpm while a plow mechanism rotates in the same direction but at reduced speeds. Solids containing about 30% moisture are transported to the small end of the bowl, and water is discharged from the larger end (8). Filtration may be used to separate the suspension instead of centrifuging (7).

The wet PVC cake from the centrifuge is dropped to a dryer. Drying techniques used include spray drying, flash-rotary drying, rotary drying, and two-stage flash drying. The polymer particle size governs the choice of drying techniques (7). The polymer is dried to 0.25 wt percent to 0.4 wt percent moisture content. The maximum allowable product temperature is 55°C, because degradation of the polymer occurs above 65°C (7,8).

The time required to dry the batch of polymer in the blend tank ranges from 5 hr to 8 hr. The exit end of the dryer is constricted to raise the air velocity high enough to entrain dry PVC particles. A cyclone separator removes the coarse particles (99.93%) and fines (99.4%). Fabric filters are provided to clean the exit air. Solid PVC recovered from the cyclone and baghouses is sized by screens and oversize particles are recycled (7).

Bulk Polymer Handling--
Dry polymer is screened to separate oversize particles. Screened PVC particles are then pneumatically conveyed to storage bins or silos. The product can either be shipped, bagged, or sent to the fabricating plant (8).

Recycle Purification--
Recovered monomer is accumulated in the recycle surge tank and continuously fed to the purification section. The purified monomer is recycled to the monomer plant.

Emulsion Polymerization

In the United States, emulsion polymerization is carried out as a batch process involving polymerization of vinyl chloride in an emulsion system (19). Emulsifiers disperse monomer droplets in water; polymerization proceeds in the aqueous phase surrounding the monomer droplets (11).

Vinyl chloride, water, emulsifying agent and initiators make up a typical recipe for emulsion polymerization (20). Many soaps and surfactants are used as emulsifiers. Natural and synthetic colloidal protective agents such as cellulose derivatives and polyvinyl alcohol are also used (11).

Relatively large amounts of emulsifiers are utilized, usually in pairs, where one agent is soluble in monomer and the other in water (11). Such system stability, combined with strong agitation, prevents coalescence of polymer particles, resulting in smaller particles than are obtained in the suspension process (11). A study was made of the relationship between the chemical nature of the emulsifier and the rate of polymerization; the properties of the resultant polymer indicated that the effect of emulsifiers on the polymerization reaction decreases as the molecular weight of the emulsifier increases (20).

Since the emulsion polymerization reaction proceeds in the aqueous phase surrounding the monomer droplets, initiators are mostly water soluble (8). Important initiators include persulfates, hydrogen peroxide, and various oxidation/reduction systems such as chlorate-bisulfite combinations.

The emulsifier and initiator (and possibly a buffer) are dissolved in cold deionized water. Air is excluded from the system as the water solution is added to the reactor (20). Measured amounts of vinyl chloride are added and agitated to form a relatively stable emulsion (20). The reaction starts when the emulsion is heated. Temperature control is important; it is achieved by circulating cold water or brine in the reactor jacket (20).

The polymerization is terminated at 90% to 95% monomer conversion. Polymerization rates decrease rapidly at higher conversion, and pressure decreases to signify completion of the reaction (20). Unreacted vinyl chloride is recycled after purification (20).

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(19) Odian, G. Principles of Polymerization. McGraw-Hill Book Company, New York, New York, 1970. pp. 279-298.

(20) Albright, L. F. Vinyl Chloride Polymerization by Emulsion, Bulk and Solution Processes. Chemical Engineering, 74(14): 145-152, 1967.

Emulsion polymerization differs from suspension polymerization in its drying operations. Emulsion resins, because of their smaller polymer particle size, are spray dried (4).

Polyvinyl chloride resins produced by emulsion polymerization retain about 2% to 5% of the emulsifier (20); hence, resins tend to be hazy and have low water absorptivity (20). Emulsion resins cost more than suspension resins, but they are used when liquid form compounds are needed, as in organosols and plastisols (20). Organisols and plastisols are used in dip coatings, slush moldings, rotational moldings and foam applications (20).

Figure 5 gives a simplified block flow diagram and Figure 6 a detailed flowsheet for the manufacture of polyvinyl chloride resins by the emulsion process.

Bulk Polymerization

Bulk polymerization, a relatively new process introduced by Produits Chimiques Pechiney-Saint-Gobain, is used to produce 6% of the PVC in the United States.

In the batch process, vinyl chloride is polymerized without the addition of other liquids (20). The process produces no major by-products, uses negligible amounts of initiators, and yields a pure product without drying. No solvents, emulsifiers or suspending agents are needed (21).

Resins manufactured by bulk polymerization are used for molding, extrusion and surfacing applications (21). Bulk resins resemble suspension resins in appearance and are homogeneous with regard to shape and size of the beads and porosity (22). They have good heat stability, improved fusion properties, high purity, and unrivaled clearness (22).

In the two-step bulk polymerization process, two reactors operate batchwise and in series (20). In the first reactor, or prepolymerizer, 7% to 12% of the vinyl chloride is polymerized at temperatures of 40°C to 70°C (23). High-speed agitation forms particles of uniform size and promotes good heat transfer with the cooled walls of the prepolymerizer (20).

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(21) Krause, A. Mass Polymerization for PVC Resins. Chemical Engineering, 72(26):72-74, 1968.

(22) Thomas, J. C. New Improved Bulk PVC Process. Hydrocarbon Processing, 47(11):192-196, 1968.

(23) Herbert, T. and S. Nagy. System Analysis of Air Pollutant Emissions from the Chemical Plastics Industry. EPA-650/2-74-106 PB 239 880. Environmental Research Center. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1974. 281 pp.

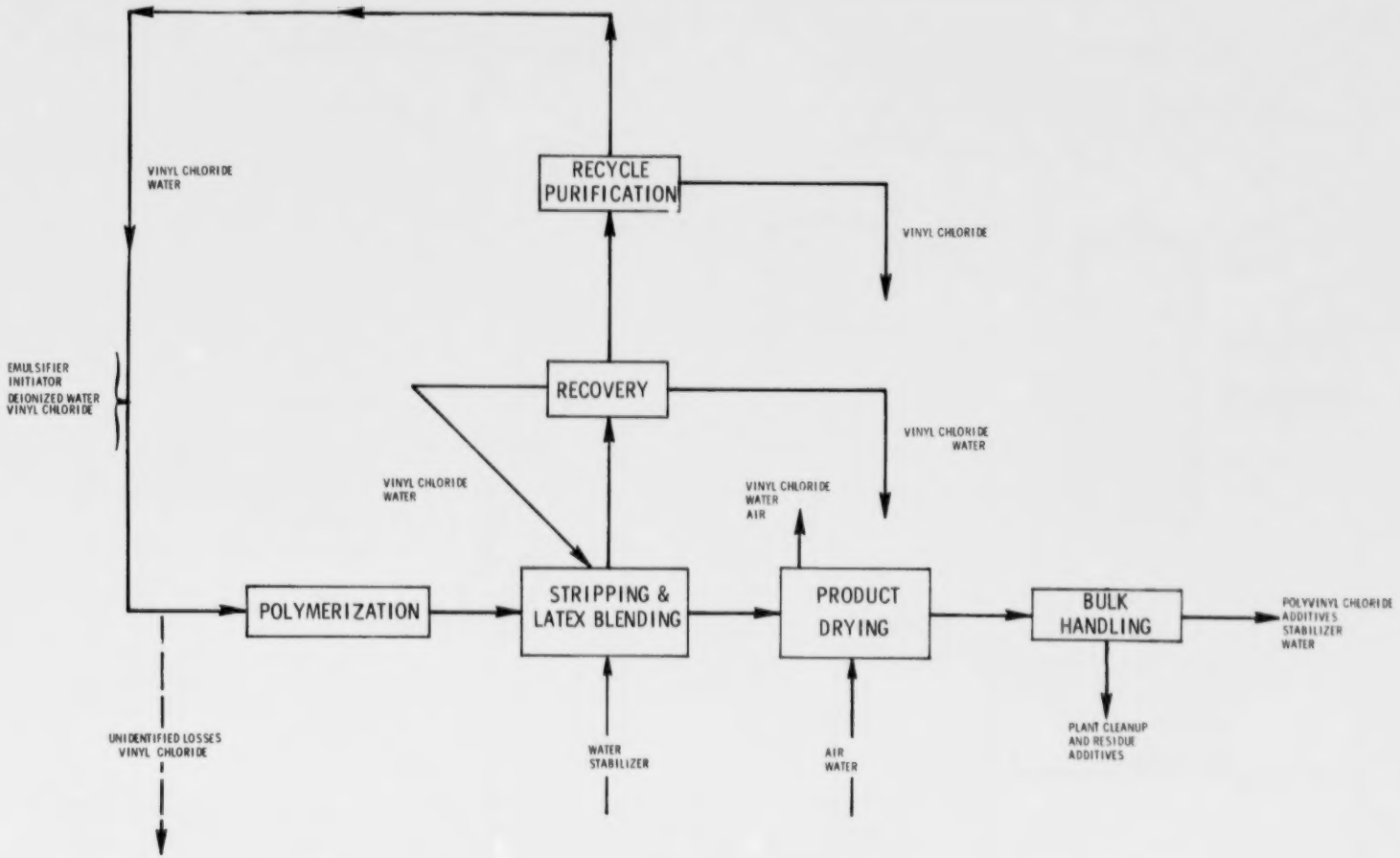

Figure 5. Block flow diagram for production of polyvinyl chloride by the emulsion process.

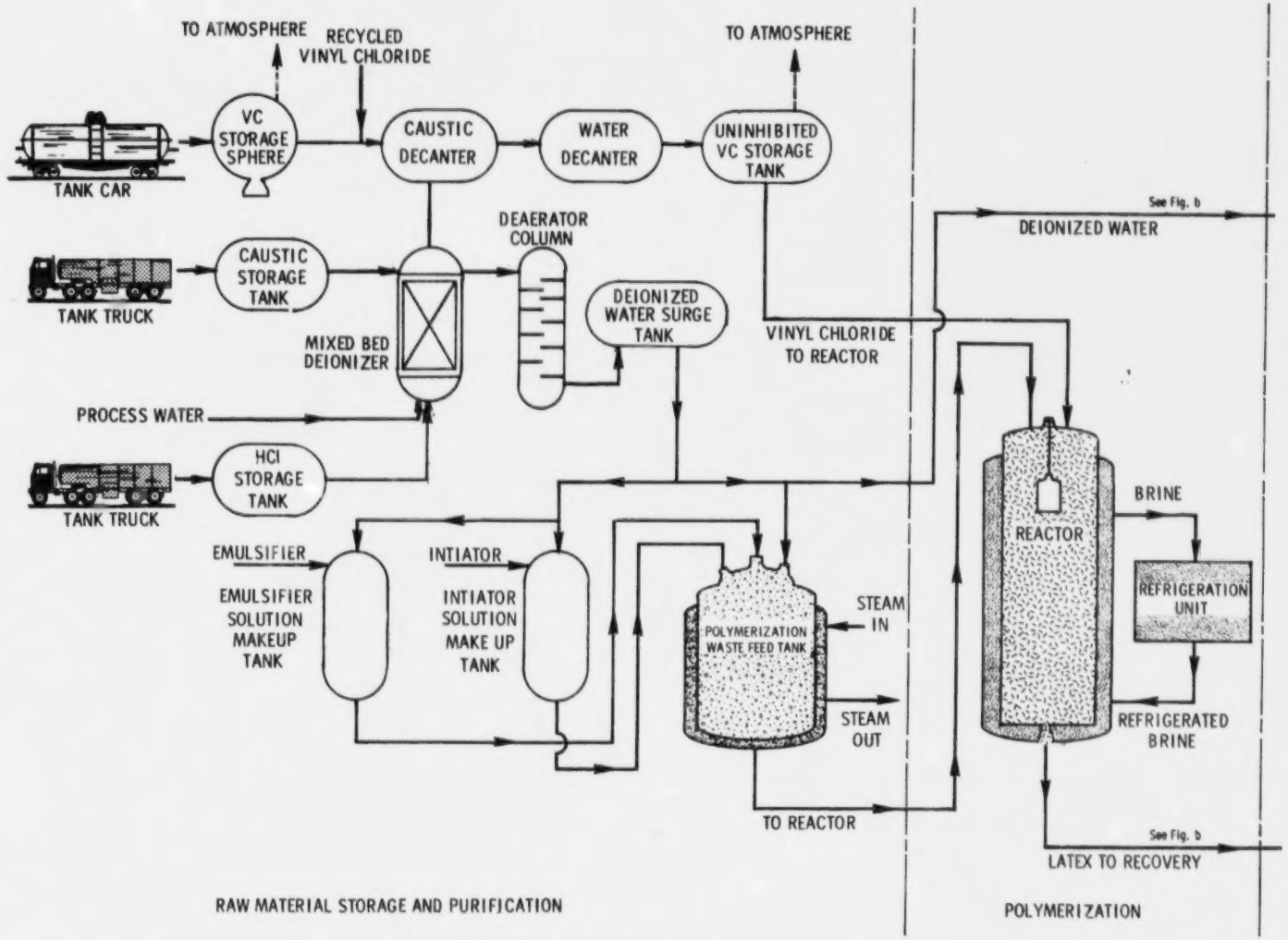

Figure 6a. Flowsheet for production of polyvinyl chloride by emulsion process.

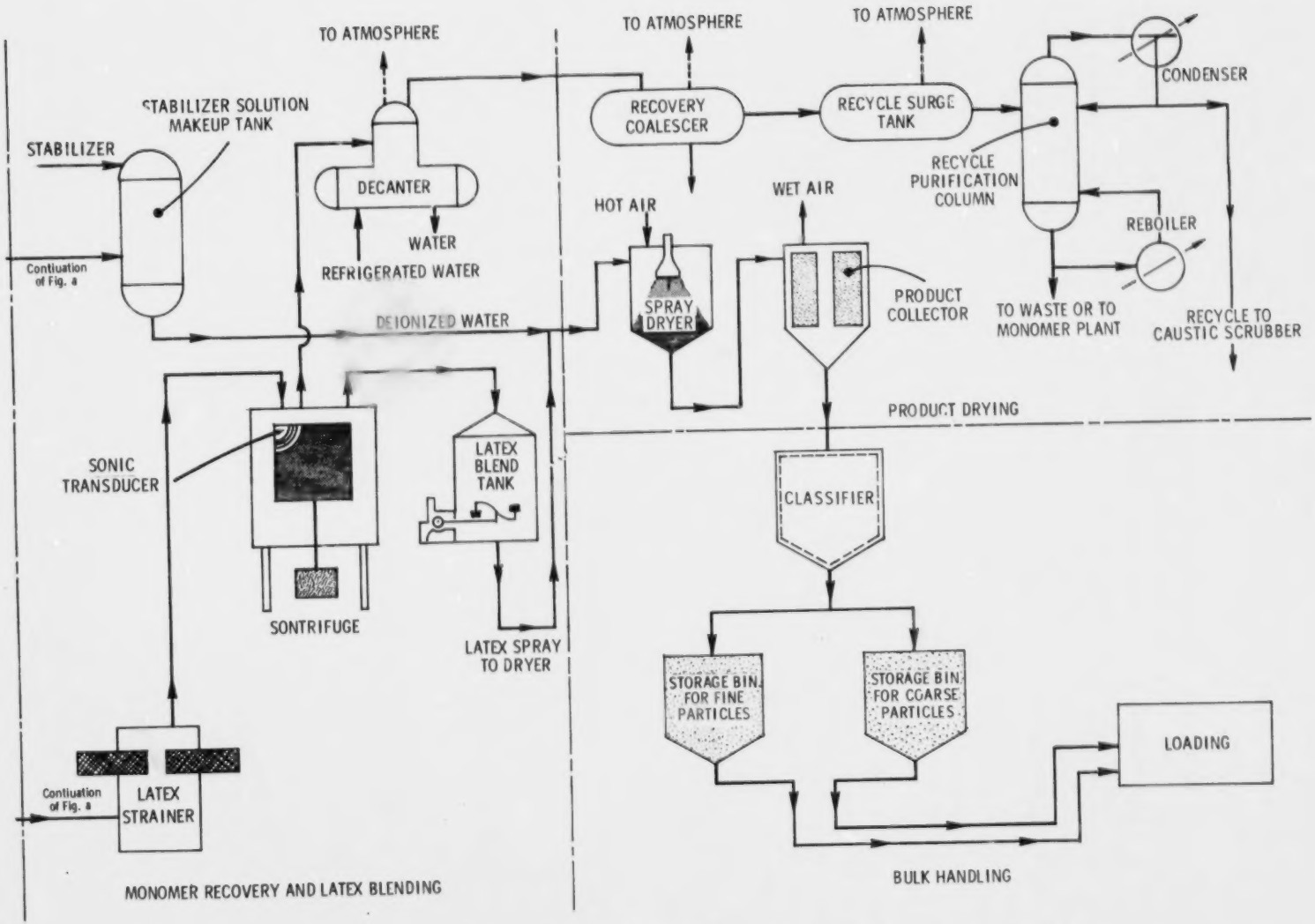

Figure 6b. Flowsheet for production of polyvinyl chloride by emulsion process.

PVC particles are first observed at approximately 4% to 8% conversion of vinyl chloride. The exact conditions at which precipitation starts depend on various operating parameters including temperature (19).

The PVC precipitate solvates five to six parts of VCM per part of PVC polymer. At 15% to 20% conversion, the liquid phase of vinyl chloride essentially disappears (20). Temperature control up to 10% conversion is provided by heat transfer from vinyl chloride liquid through the reactor walls (20). It has been reported that 10% of the vinyl chloride has polymerized after three hours, the time depending upon the temperature and amount of initiator (4).

The suspension of PVC in VCM liquid is then transferred to the large reactor, or polymerizer. The polymerizer is stirred with ribbon blenders consisting of two or three ribbons wound on whorls of different diameters (4) that turn in opposite directions.

As the reaction mixture changes from slurry, to stocky solid, to dry particles, it is important to prevent undesired agglomeration of PVC particles and to control temperature. The speed of agitation is reduced as polymerization proceeds. The second stage requires 10 hr to 15 hr for completion of the reaction (4).

Figure 7 is a block flow diagram and Figure 8 a detailed flowsheet of the manufacture of PVC by the bulk process.

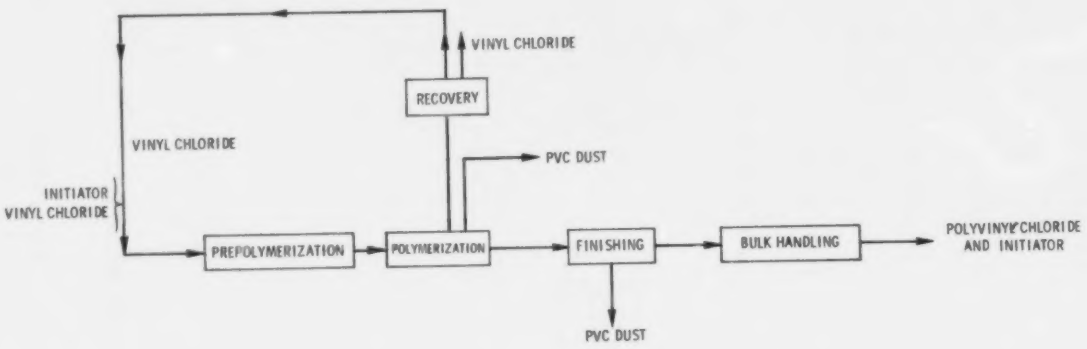

Figure 7. Block flow diagram for production of polyvinyl chloride by the bulk processes.

Solution Polymerization

In the United States, only one company uses solution polymerization for the manufacture of polyvinyl chloride. Solution polymerization is the only continuous process for producing PVC, and most resins produced are copolymers of polyvinyl chloride (75% to 90%) and polyvinyl acetate (10% to 25%) (4).

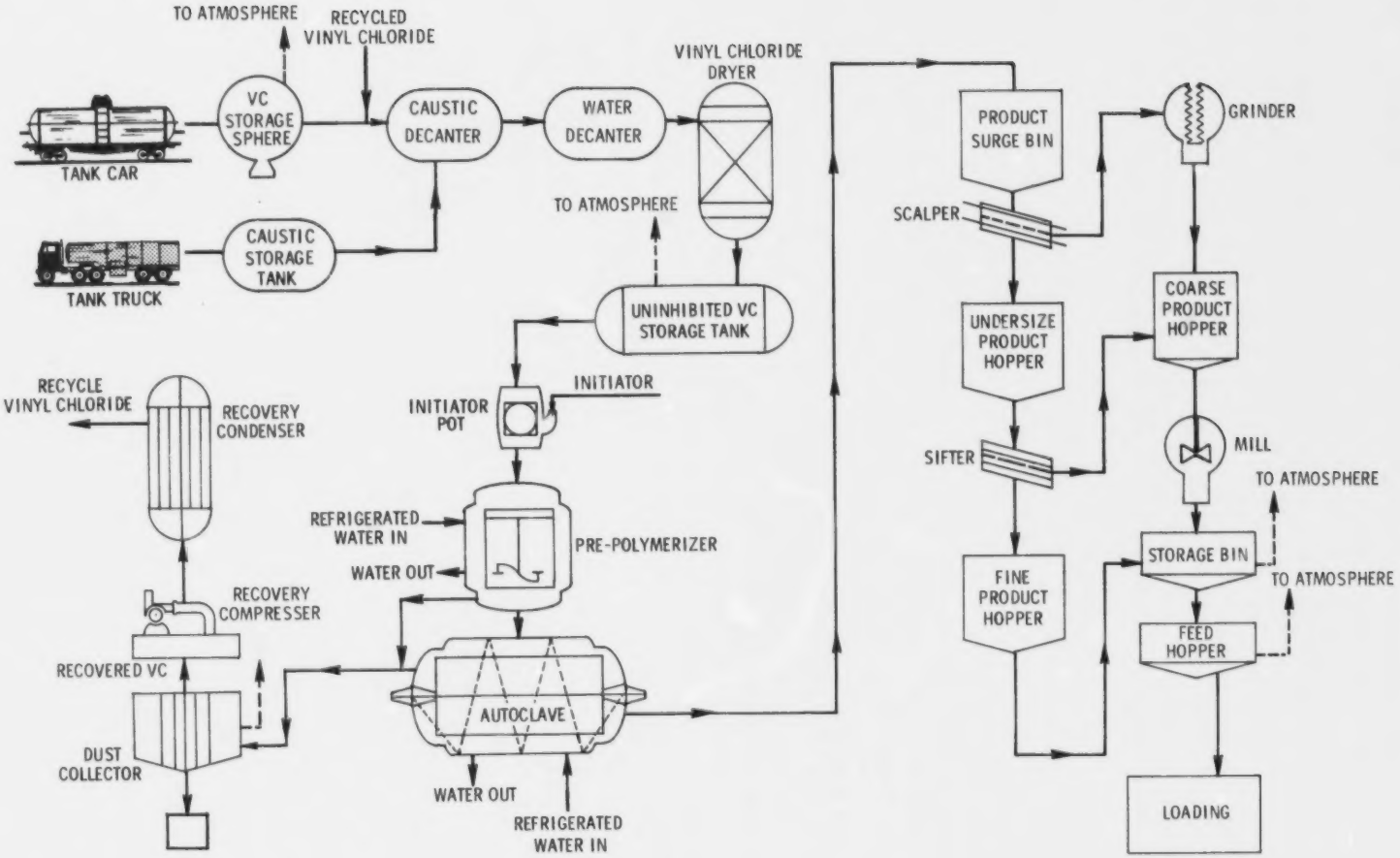

Figure 8. Flowsheet for production of polyvinyl chloride by the bulk process.

Solution polymerization of PVC is not a true solution polymerization, since the polymer precipitates. It is sometimes called precipitation polymerization (20).

Polymerization is carried out at 40°C to 55°C with an initiator in a liquid medium for 12 hr to 18 hr (22). Vinyl chloride and its comonomers are soluble in the solvent, but the polymer is not (24). Suitable solvents used for vinyl resins are aliphatic alcohols, aliphatic hydrocarbons, aromatic hydrocarbons, aliphatic ketones, aliphatic esters, and chlorinated hydrocarbons (24, 25). The character of the resulting resin depends on the solvent used (7).

As the reaction proceeds, the polymer appears as a powder suspended in the solvent. As the polymer precipitates from solution, autoacceleration occurs because of monomer occluded in the precipitates (11). The resin is removed by circulating the slurry through a filter press into a settling tank. The filter cake is dried by flash evaporation, and recovered monomer and solvent are recycled (4).

Solution polymerization of vinyl chloride proceeds as in bulk polymerization. With a granular precipitate and rate acceleration from the start of the reaction[a], solution polymerization obviates many of the disadvantages of the bulk process (19). Temperature control is easier and, because of a decreased viscosity, stirring is efficient. Problem areas associated with solution polymerization include proper solvent selection to avoid chain transfer, and careful removal of solvent from product to avoid contamination.

PVC resins obtained by solution polymerization are relatively pure, because emulsifiers or suspending agents are not required (20). Another advantage of solution polymerization is simplified product recovery, because water is not used in the process (20).

A block flow diagram and a flowsheet for the solution polymerization process are shown in Figures 9 and 10, respectively.

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[a] Information obtained from EPA files concerning private communi cation between E. M. Smith, Continental Oil Company, Ponca City, Oklahoma, and D. Goodwin, EPA, Research Triangle Park, North Carolina, 12 July 1974.

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(24) Douglas, S. D. Process for Producing Vinyl Resins. U.S. Patent 2,075,429 (to Union Carbide), March 30, 1937.

(25) Reid, E. W. Process for Producing Vinyl Resins. U.S. Patent 2,064,565 (to Union Carbide), December 15, 1936.

(26) Reid, E. W. Vinyl Resins. U.S. Patent 1,935,577 (to Union Carbide), November 14, 1933.

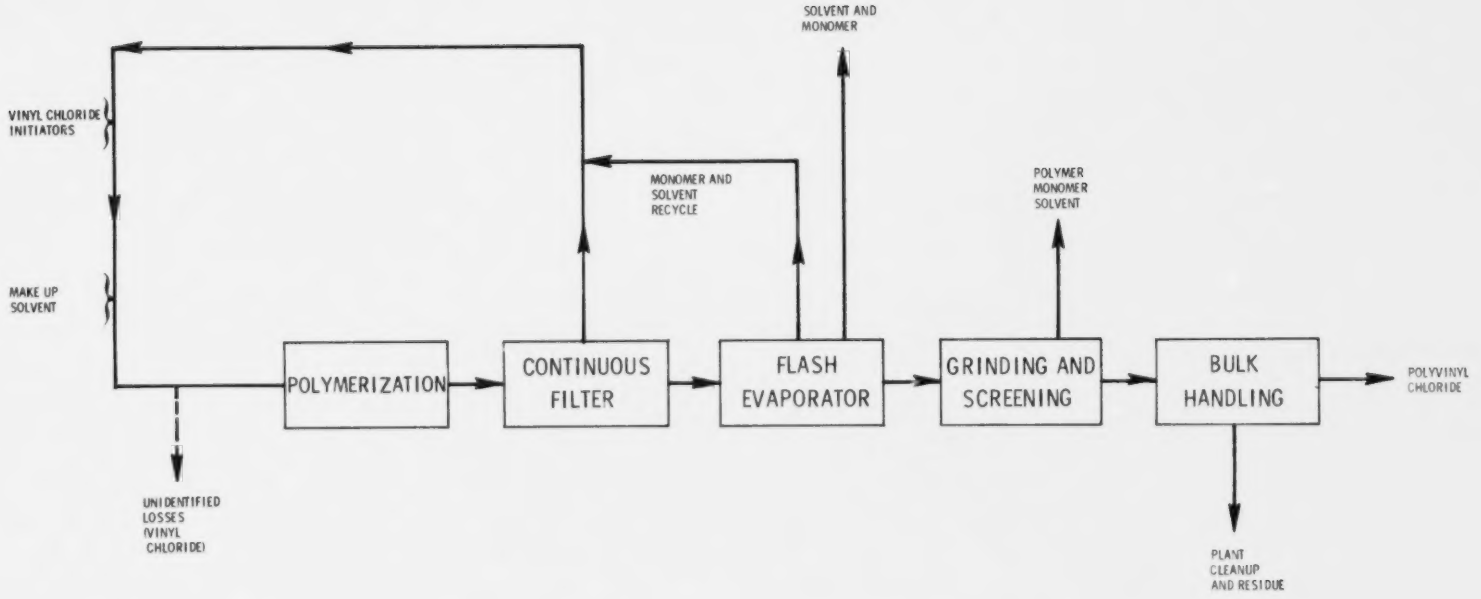

Figure 9. Block flow diagram for the production of polyvinyl chloride by the solution process.

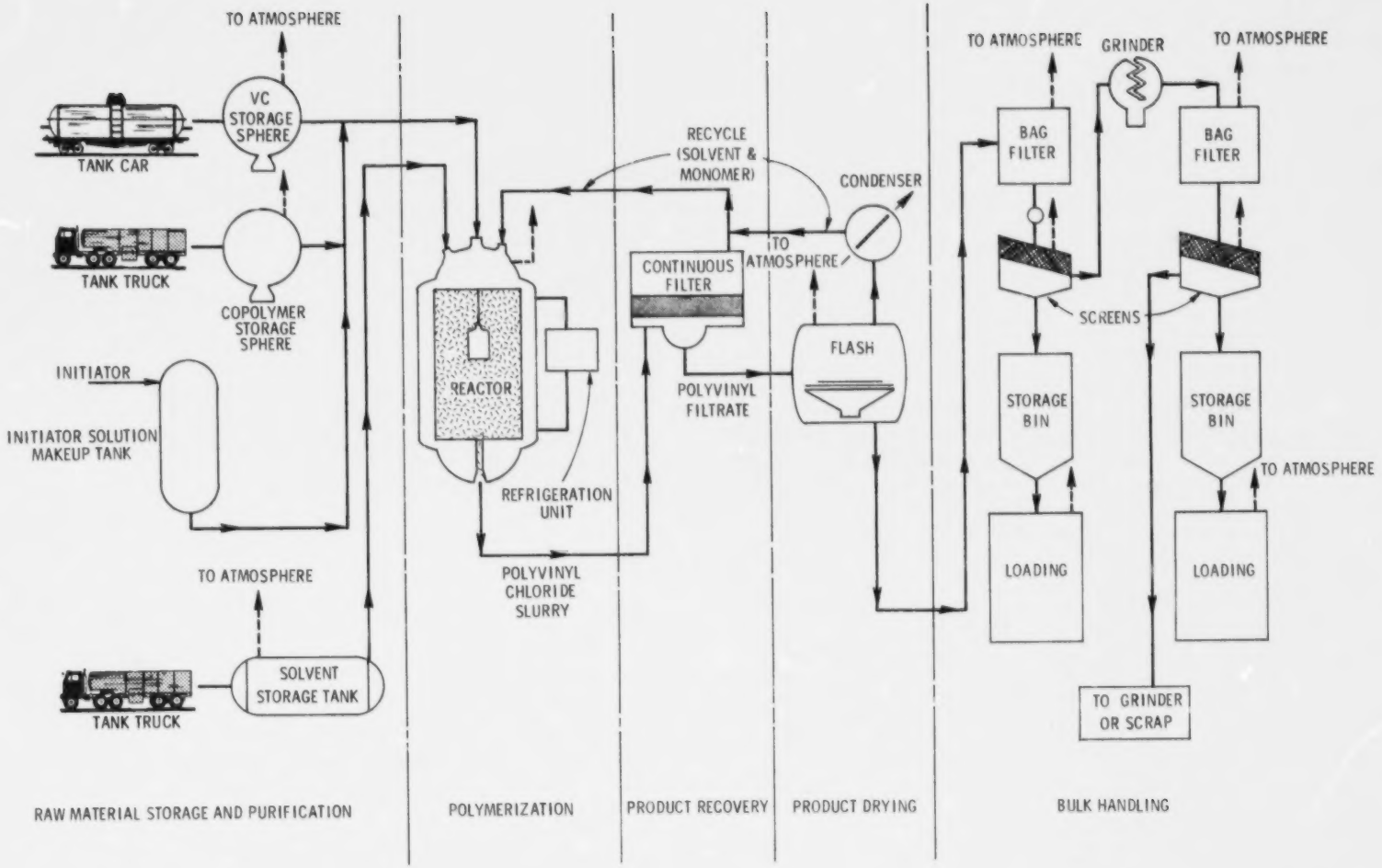

Figure 10. Flowsheet for production of polyvinyl chloride by the solution process.

MATERIALS FLOW

A simplified material balance for the suspension polymerization process for a representative plant with a production rate of 68 x 10^3 metric tons/yr is shown in Figure 11.

GEOGRAPHICAL DISTRIBUTION

Table 7 provides the locations and capacities of PVC manufacturing plants. Based on capacities of PVC manufacturers, the average plant capacity was calculated to be 68 x 10^3 metric tons/yr. Figure 12 shows the locations of the U.S. facilities.

TABLE 7. LOCATIONS AND CAPACITIES OF POLYVINYL CHLORIDE MANUFACTURING PLANTS

Producing company	Plant location	Capacity, 10^3 metric tons/yr
Air Products, Inc.	Calvert City, KY	61.23
	Pensacola, FL	34.02
American Chemical Corp.	Long Beach, CA	68.04
Borden, Inc.	Illiopolis, IL	63.50
	Leominster, MA	81.65
	Springfield, MA	31.75
Continental Oil Co.	Aberdeen, MS	117.93
	Oklahoma City, OK	99.79
Diamond Shamrock Corp.	Delaware City, DE	45.36
	Deer Park, TX	122.47
Ethyl Corp.	Baton Rouge, LA	81.65
Firestone Tire Co.	Perryville, MD	104.33
	Pottstown, PA	122.47
General Tire Co.	Ashtabula, OH	56.70
B. F. Goodrich Co.	Avon Lake, OH	117.93
	Henry, IL	99.79
	Long Beach, CA	52.16
	Louisville, KY	65.77
	Pedricktown, NJ	63.50
Goodyear Tire Co.	Niagara Falls, NY	45.36
	Plaquemine, LA	49.63
Great American Chemical Corp.	Fitchburg, MA	18.14
Keysor-Century Corp.	Saugus, CA	15.88
Occidental Petroleum	Burlington, NJ	76.20
	Hicksville, NY	6.80
Olin Corp.	Assonet, MA	68.04
Pantasote Co.	Passaic, NJ	27.22
	Point Pleasant, WV[a]	43.09
Robintech, Inc.	Painesville, OH	113.40
Stauffer Chemical Co.	Delaware City, DE	79.38
Tenneco Chemicals, Inc.	Burlington, NJ	74.84
	Flemington, NJ	31.75
Union Carbide Corp.	South Charleston, WV	72.57
	Texas City, TX	136.08
Uniroyal, Inc.	Painesville, OH	48.99
AVERAGE CAPACITY		68.44

[a]Pantasote's Point Pleasant, West Virginia plant is 50% owned by General Tire Company.

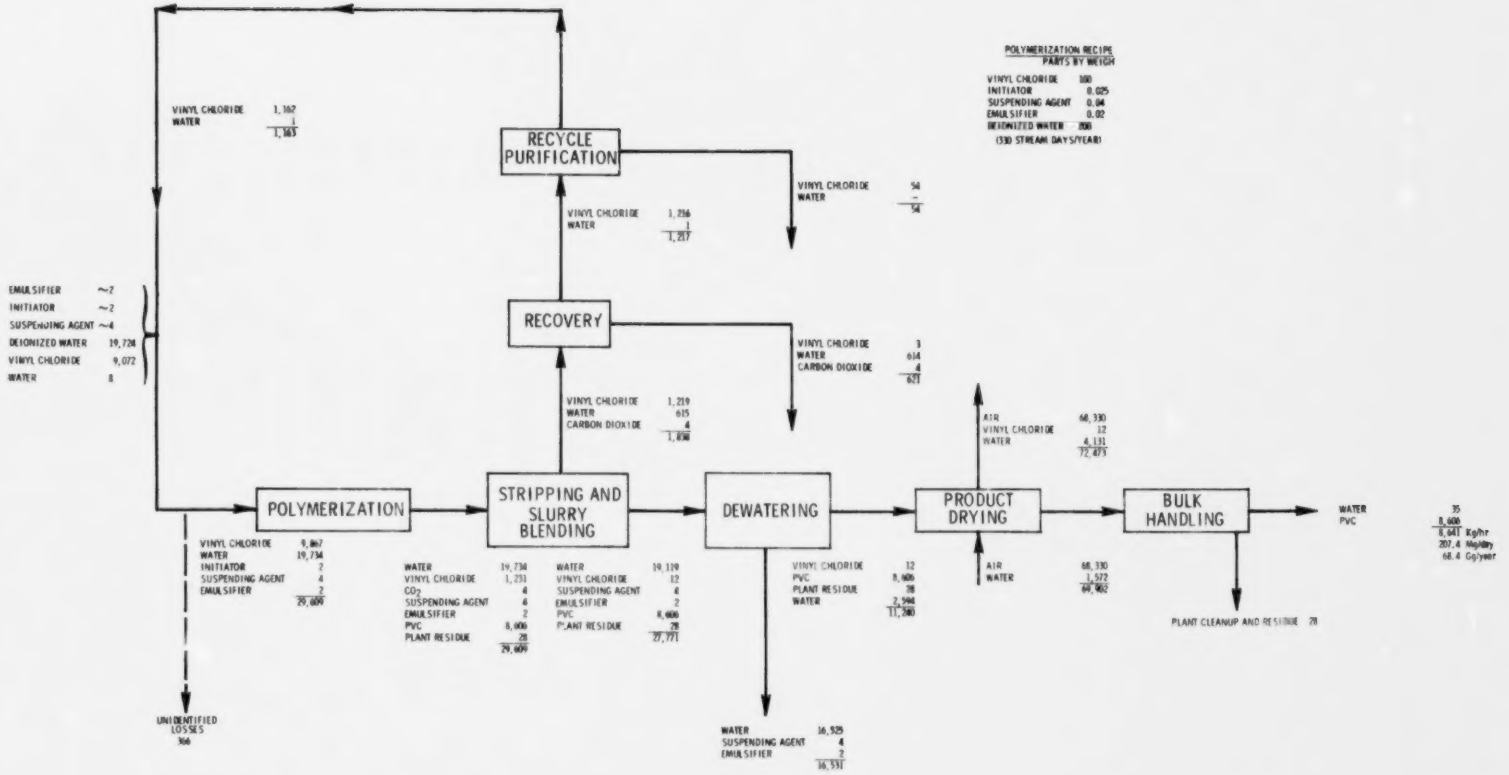

Figure 11. Simplified material balance for suspension process.

Figure 12. Polyvinyl chloride plant locations.

SECTION 4

EMISSIONS

LOCATIONS AND DESCRIPTIONS

A typical polyvinyl chloride plant has 12 sources of vinyl chloride monomer and particulate polyvinyl chloride emissions. The emission points are identified in Table 8. Information in this section was obtained from EPA files of data reported by operating companies during 1974. The data were obtained only partially through actual field sampling; most came through material balance and engineering estimates.

TABLE 8. POINTS OF EMISSION AT A REPRESENTATIVE POLYVINYL CHLORIDE PLANT

Identification point in Figure 3	Description
A	Reactor safety relief valves
B	Reactor entry purge
C	Stripper jets
D	Monomer recovery condenser vent
E	Slurry blend tank vents
F	Centrifuge vent
G	Dryer discharge
H	Storage silos
I	Bulk loading
J	Bagger vent
K	Storage tanks
L	Fugitive emissions

Reactor Safety Relief Valves

Reactor safety relief valves are an intermittent source of emissions[a] with reported discharges occurring from 3 to 20 times per

[a] Information obtained from EPA files concerning private communication between E. M. Smith, Continental Oil Company, Ponca City, Oklahoma, and D. Goodwin, EPA, Research Triangle Park, North Carolina, 12 July 1974.

year (27). Power failure, operator error and equipment failure will cause venting by pressure relief valves and rupture discs (27). Manual venting is also used to reduce pressure, thereby preventing greater losses.[a]

Atmospheric emissions from venting of the polymerizer consist of VCM, PVC, or some combination thereof, depending upon the stage of VCM conversion.[a] Emissions from this source range between 0.6 g/kg and 2.2 g/kg and discharge at a height of 15 m[a] (4).

Reactor Entry Purge

The reactor is purged with air (27) after PVC slurry has been transferred to the slurry blend tank[a] and after most of the VCM has been removed by vacuum or by water displacement to the monomer recovery system (4). Until recently it was necessary to open reactors after each batch to remove PVC buildup on the reactor walls (4). Plants are now reducing VCM exposure as much as 90% by reducing work forces through automation, and by improved cleaning techniques (28). Emissions range from 0.8 g/kg to 5.0 g/kg and are emitted at a height of 15 m (4).

Stripper Jets

Emissions from stripper jets are intermittent.[a] After polymerization, unreacted VCM is removed by venting the reactor to a recovery system. Some vinyl chloride remains in the water or trapped in the PVC particles. This residual vinyl chloride is stripped in the reactor or in a second vessel called the stripper (28) where stripping is carried out in vacuum and/or by contact with steam (27).

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[a]Information obtained from EPA files concerning private communication between H. C. Holbrook, B. F. Goodrich Chemical Company, Cleveland, Ohio, and D. Goodwin, EPA, Research Triangle Park, North Carolina, 17 June 1974.

(27) Evans, L. B., and L. L. Beck. The Vinyl Chloride and PVC Industry Emissions and Control Techniques. Draft copy of report. U.S. Environmental Protection Agency. Emission Standards and Engineering Division, Industrial Studies Branch, July 23, 1974.

(28) PVC Plants are Ready to Pass First Test. Chemical Week, 116(19):49-50, 1975.

Stripping operations are important; control (28) of emissions from the slurry blend tank, the centrifuge, the dryer and the bulk storage silos is dependent upon effective removal of residual vinyl chloride trapped in the PVC granule (4).

Atmospheric emissions consist of inerts and vinyl chloride (27). The emissions range between 0.5 g/kg and 12.3 g/kg (4).

Monomer Recovery Condenser Vent

The monomer recovery condenser vent is an intermittent emission source by nature.[a] Recycled vinyl chloride is treated in a two-stage compression system where the monomer is dewatered and purified (12, 15). Inert gas, water vapor, and VCM are discharged to the atmosphere.[a] The emissions from this source range between 3.1 g/kg and 15.0 g/kg and exhaust at a height of 18 m[a] (4).

Slurry Blend Tank Vents

Slurry blend tank vents are a continuous source of emissions[a] resulting from the continuous purging of the vapor space in the atmospheric pressure slurry blend tanks with fresh air.[a] In the slurry tank, vinyl chloride is released from the PVC granules where it was trapped (27).

The emission rate for this source ranges from 2.5 g/kg to 5.7 g/kg (27).

Centrifuge Vent

Emissions from the centrifuge vent are continuous. The centrifuge separates the slurry into wet solids containing 75% to 77% PVC in water (12). Some of the vinyl chloride trapped within the PVC granules is released (27). The atmospheric emissions from the centrifuge vent consist of water vapor, air, VCM and PVC resin.

The rate of emission varies between 0.04 g/kg and 1.3 g/kg (4), exhausted at a height of 17 m.[a]

Dryer Discharge

Dryer discharges are a continuous emission source.[a] The wet polymer contains about 20% to 25% moisture (15) and is dried using air at temperatures ranging from 60°C to 66°C (15). Atmospheric emissions from the dryer exhaust consist of air, water vapor, vinyl chloride and polyvinyl chloride.[a]

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[a] Information obtained from EPA files concerning private communication between H. C. Holbrook, B. F. Goodrich Chemical Company, Cleveland, Ohio, and D. Goodwin, EPA, Research Triangle Park, North Carolina, 17 June 1974.

Emissions from this source range between 2.0 g/kg and 25.6 g/kg (27).

Storage Silos

Storage silos are a continuous source of emissions. The polymer stored in the silos is frequently mixed by passing dry air through the silos. This prevents moisture condensation and the buildup of explosive concentrations of VCM (27).

Atmospheric emissions consist of air, VCM, and PVC. The rate of emission varies between 0.2 g/kg and 1.7 g/kg (27) emitted at a height of 21 m.

Bulk Loading

A continuous discharge of air and particulate PVC takes place during loading operations. The emission rate is estimated to be 0.4 g/kg.

Bagger Vent

The vent from the bagging operations is a continuous source of particulate emissions. This stream, containing PVC and air, is ducted to a baghouse for recovery of the solid product.[a] The emission rate for this source is estimated to be 0.2 g/kg.

Storage Tanks

The emissions from storage tank vents have been estimated to be 0.6 g/kg.

Fugitive Emissions

Leaks occurring from pressure relief valves, pumps, compressors, agitator seals, loading and unloading of monomer, valve stems, flanges, unrepaired purging equipment and samples for laboratory analysis are defined as fugitive emissions (4). There may be as many as 600 points of fugitive emissions at a typical PVC plant (4).

The vinyl chloride emission rate from this source ranges from 6.2 6.2 g/kg to 17.5 g/kg (27).

EMISSION FACTORS

VCM emission factors for the four processes used to produce polyvinyl chloride are given in Table 9.

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[a] Information obtained from EPA files concerning private communication between H. C. Holbrook, B. F. Goodrich Chemical Company, Cleveland, Ohio, and D. Goodwin, EPA, Research Triangle Park, North Carolina, 17 June 1974.

TABLE 9. VINYL CHLORIDE EMISSION FACTORS FOR POLYVINYL CHLORIDE PROCESSES (4)

Process type	VCM emission factors, g/kg
Suspension process	35.5
Emulsion process	60.1
Bulk process	24.2
Solution process	17.8

Table 10 lists the contributions of PVC-producing plants in the United States to national point source emissions (1) of criteria pollutants. Table 11 lists contributions from PVC production to state emissions of criteria pollutants. Since production data by state was not readily available, plant capacities were used. Table 12 lists TLV®, atmospheric reactivity and health effects of each species emitted from a PVC manufacturing plant.

TABLE 10. POLYVINYL CHLORIDE INDUSTRY CONTRIBUTIONS TO NATIONAL STATIONARY SOURCE EMISSIONS OF CRITERIA POLLUTANTS

Material emitted	Total national emissions (1), 10^6 metric tons/yr	Emissions from the PVC industry	
		10^3 metric tons/yr	Percent of national emissions
Hydrocarbons (vinyl chloride, phenol stabilizer, ethyl chloride, butadiene, vinylidene chloride, acetaldehyde, acetylene, propylene, vinylacetylene, ethylene, ethylene dichloride, chloroprene, vinyl bromide)	25	85	0.34
Particulate (polyvinyl chloride)	18	18	0.10
Sulfur oxides	30	5.5×10^{-4}	2×10^{-6}

TABLE 11. POLYVINYL CHLORIDE INDUSTRY CONTRIBUTIONS TO STATE EMISSIONS OF CRITERIA POLLUTANTS

State	Material emitted[a]	State emissions (1), 10^3 metric tons/yr	PVC emissions	
			metric tons/yr	Percent
New Jersey	Vinyl chloride	819.5	9,450	1.15
	PVC	151.8	2,370	1.56
Massachusetts	Vinyl chloride	440.5	5,845	1.33
	PVC	96.16	855	0.09
Ohio	Vinyl chloride	1,153	10,620	0.92
	PVC	1,766	3,030	0.17
California	Vinyl chloride	2,161	2,145	0.10
	PVC	1,006	1,505	0.15
West Virginia	Vinyl chloride	116.2	8,030	6.91
	PVC	213.7	380	0.18
Illinois	Vinyl chloride	1,826	7,090	0.39
	PVC	1,143	1,775	0.16
Texas	Vinyl chloride	2,219	6,980	0.31
	PVC	549.4	1,820	0.33
Delaware	Vinyl chloride	63.89	2,770	4.34
	PVC	36.81	2,370	0.78
Louisiana	Vinyl chloride	1,920	6,915	0.36
	PVC	380.6	715	0.19
New York	Vinyl chloride	1,262	2,055	0.16
	PVC	160	150	0.09
Kentucky	Vinyl chloride	326.3	7,380	2.26
	PVC	546.2	1,295	0.24
Florida	Vinyl chloride	619.9	1,075	0.17
	PVC	226.5	490	0.22
Maryland	Vinyl chloride	295.9	1,860	0.63
	PVC	494.9	510	0.10
Oklahoma	Vinyl chloride	341.4	3,660	1.07
	PVC	93.6	65	0.07
Mississippi	Vinyl chloride	196	4,185	2.14
	PVC	168.4	885	0.52
Pennsylvania	Vinyl chloride	891.8	4,150	0.47
	PVC	1,811	365	0.02

[a]Vinyl chloride hydrocarbon emission; PVC particulate emission.

TABLE 12. CHARACTERISTICS OF EMISSIONS FROM A REPRESENTATIVE POLYVINYL CHLORIDE PLANT

Compound	TLV, (29) g/m^3	Atmospheric reactivity	Health effects
Vinyl chloride	0.0026	Contributes to photochemical smog	A recognized carcinogen
Polyvinyl chloride	0.1090	Stable	Suspected carcinogen
Ethylene	1.25	Contributes to photochemical smog	Moderate irritant
Propylene	1.88	Contributes to photochemical smog	Moderate asphyxiant
Acetylene	1.16	Contributes to photochemical smog	Moderate asphyxiant
Butadiene	2.20	Contributes to photochemical smog	Moderate irritant and asphyxiant
Ethylene dichloride	0.20	Contributes to photochemical smog	Sharp irritant and asphyxiant
Vinylacetylene	0.0480	Contributes to photochemical smog	Simple irritant and asphyxiant
Vinyl bromide	1.10	Contributes to photochemical smog	Moderate irritant and asphyxiant
Vinylidene chloride	0.004	Contributes to photochemical smog	Details unknown
Acetaldehyde	0.18	Contributes to photochemical smog	Sharp irritant and asphyxiant
Ethyl chloride	2.60	Contributes to photochemical smog	Simple irritant and moderate asphyxiant
Chloroprene	0.09	Contributes to photochemical smog	Sharp irritant and asphyxiant
Hydrogen chloride	0.007	Contributes to chloride formation	Sharp irritant and asphyxiant
Sulfur oxides	0.013	Contributes to sulfate formation	Sharp irritant and asphyxiant
Phenol (stabilizer)	0.02	Contributes to photochemical smog	Sharp irritant and asphyxiant

(29) TLVs® Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH for 1976. American Conference of Governmental Industrail Hygienists. Cincinnati, Ohio, 1976. 94 pp.

DEFINITION OF REPRESENTATIVE SOURCE

A representative plant for polyvinyl chloride manufacture was defined in order to determine source severity. Factors considered include polymerization process, plant capacity, polymer produced, vinyl chloride emission factor, PVC emission factor, emission height for VCM emissions, emission height for PVC emissions, maximum ground level concentration, and source severity. Table 13 gives a summary of data used to determine a representative plant. Table 14 summarizes the data for a representative plant.

Table 15 gives the representative PVC manufacturing plant emission factors for vinyl chloride and polyvinyl chloride. Table 16 lists the emissions from the 12 major sources at a representative PVC plant. One of these major sources, fugitive emissions, is further broken down into seven categories.

ENVIRONMENTAL EFFECTS

Maximum Ground Level Concentration

The maximum ground level concentration, χ_{max}, for materials emitted from each of 12 major points of emission for a polyvinyl chloride plant were estimated by a Gaussian plume dispersion method. χ_{max}, in g/m^3, was calculated using the equation:

$$\chi_{max} = \frac{2\,Q}{\pi h^2 e \bar{u}} \qquad (1)$$

where Q = emission rate, g/s
h = effective emission height, m
e = 2.72
π = 3.14
$\bar{u}$ = average wind speed = 4.47 m/s

Time-Averaged Maximum Ground Level Concentration

$\bar{\chi}_{max}$ is the maximum ground level concentration averaged over a given period of time. The averaging time is 24 hr for noncriteria pollutants (chemical substances). For criteria pollutants, averaging times are the same as those used in the primary ambient air quality standard; (i.e., 3 hr for hydrocarbons and 24 hr for particulates). The relationship between χ_{max} and $\bar{\chi}_{max}$ is expressed as:

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{t_o}{t}\right)^{0.17} \qquad (2)$$

where t_o = "instantaneous" averaging time = 3 min
t = averaging time for ambient air quality standard

TABLE 13. POLYVINYL CHLORIDE - SUMMARY OF PLANT DATA - I

Producing company	Plant location	Population density, persons/km²	Polymerization process[a]	Plant capacity, 10^3 metric tons/yr (homopolymer) (2)	Polymer produced[a]	Vinyl chloride emission factor, g/kg	Polyvinyl chloride emission factor, g/kg	VCM emission height, m	PVC emission height, m	χ_{max} (VCM), g/m³
Air Products, Inc.	Calvert City, Kentucky	25.1	S	61.23	H,C	37.37[b]	7.41[b]	26.64 ± 6.84[b]	14.10 ± 9.04[b]	6.26×10^{-1}
	Pensacola, Florida	116.6	S	34.02	H	31.65[b]	14.40[b]	15.58 ± 11.75[b]	18.29 ± —[b,c]	7.37×10^{-1}
American Chemical Corp.	Long Beach, California	661.8	S	68.04	H,C	4.72[d]	12.23[d]	—[c,d]	—[c,d]	2.22×10^{-1}[e]
Borden, Inc.	Illiopolis, Illinois	69.9	S	63.50	H,C	25.70[f]	1.26[f]	17.43 ± 9.27[f]	26.21 ± 5.25[f]	8.92×10^{-3}
	Leominster, Massachusetts	161.8	S	81.65	H,C	25.77[f]	1.20[f]	—[c,f]	—[c,f]	1.46×10^{-2}[e]
	Springfield, Massachusetts	281.5	S,E	31.75	H	—[c,f]	—[c,f]	—[c,f]	—[c,f]	7.79×10^{-3}[e]
Continental Oil Co.	Aberdeen, Mississippi	16.6	S	117.93	H	—[c,g]	—[c,g]	—[c,g]	—[c,g]	8.56×10^{-3}[e]
	Oklahoma City, Oklahoma	279.9	S	99.79	H	36.66[h]	0.65[h]	—[c,h]	—[c,h]	2.53×10^{-2}[e]
Diamond Shamrock Corp.	Delaware City, Delaware	340.5	S,E	45.36	H	—[c,i]	2.20[i]	6.86 ± 0.57[i]	24.38 ± 5.98[i]	5.68×10^{-2}
	Deer Park, Texas	386.1	S,E	122.47	H	3.41[i]	6.55[i]	17.43 ± 13.12[i]	22.24 ± 4.62[i]	2.28×10^{-1}
Ethyl Corp.	Baton Rouge, Louisiana	232.8	S,E	81.65	H	—[c,j]	—[c,j]	—[c,j]	—[c,j]	2.00×10^{-2}[e]
Firestone Tire Co.	Perryville, Maryland	56.0	S,E	104.33	H	17.85[k]	4.88[k]	18.51 ± 5.93[k]	21.39 ± 6.54[k]	9.03×10^{-3}[e]
	Pottstown, Pennsylvania	135.1	S,E	122.47	H,C	33.90[l]	2.98[l]	—[c,l]	—[c,l]	2.87×10^{-2}[e]
General Tire Co.	Ashtabula, Ohio	53.3	S	56.70	H	9.96[m]	—[c,m]	—[c,m]	—[c,m]	3.91×10^{-3}[e]
B. F. Goodrich Co.	Avon Lake, Ohio	199.2	S,E,B	117.93	H,C	45.70[n]	20.00[n]	17.65 ± 4.34[n]	16.88 ± 0.94[n]	2.87×10^{-2}
	Henry, Illinois	9.3	S,E,B	99.79	H	54.70[n]	17.00[n]	22.56 ± 0.00[n]	22.56 ± 0.00[n]	1.78×10^{-2}
	Long Beach, California	661.8	S,E,B	52.16	H	29.00[n]	10.60[n]	11.20 ± 1.77[n]	40.00 ± —[c,n]	2.00×10^{-2}
	Louisville, Kentucky	709.3	S,E,B	65.77	H,C	77.40[n]	12.80[n]	12.12 ± 2.90[n]	10.41 ± 1.60[n]	5.74×10^{-2}
	Pedricktown, New Jersey	63.7	S,E,B	63.50	H	36.30[n]	15.20[n]	14.10 ± 6.32[n]	18.49 ± 4.53[n]	1.93×10^{-2}
Goodyear Tire Co.	Niagara Falls, New York	169.1	S,B	45.36	H	40.00[o]	2.15[o]	10.95 ± 1.50[o]	16.75 ± 3.36[o]	2.51×10^{-2}
	Plaquemine, Louisiana	18.9	S,B	49.63	H	80.93[p]	2.06[p]	16.38 ± 7.25[p]	20.75 ± 3.63[p]	2.39×10^{-2}
Great American Chemical Corp.	Fitchburg, Massachusetts	161.8	S	18.14	H	10.96[q]	0.45[q]	—[c,q]	—[c,q]	1.38×10^{-3}[e]
Keysor-Century Corp.	Saugus, California	661.8	S	15.88	H,C	19.53[r]	—[c,r]	—[c,r]	—[c,r]	2.15×10^{-3}[e]
Occidental Petroleum Corp.	Burlington, New Jersey	152.9	B	76.20	H	13.21[s]	2.62[s]	17.78 ± 8.42[s]	18.90 ± 10.25[s]	5.29×10^{-3}
	Hickaville, New York	1,887.6	S	6.80	H,C	—[c,s]	—[c,s]	—[c,s]	—[c,s]	1.67×10^{-3}[e]
Olin Corp.	Assonet, Massachusetts	307.3	S	68.04	H,C	—[c,t]	—[c,t]	—[c,t]	—[c,t]	1.67×10^{-2}[e]
Pantasote Co.	Passaic, New Jersey	1,646.7	S	27.22	H,C	48.77[u]	0.05[u]	9.65 ± 5.91[u]	14.48 ± 29.31[u]	2.37×10^{-2}
	Point Pleasant, West Virginia	21.2	S	43.09	H,C	83.09[u]	0.05[u]	10.16 ± 7.12[u]	16.00 ± 36.07[u]	5.76×10^{-2}
Robintech, Inc.	Painesville, Ohio	326.3	S	113.40	H	35.10[v]	1.25[v]	13.49 ± 2.90[v]	19.87 ± 2.22[v]	2.63×10^{-2}
Stauffer Chemical Co.	Delaware City, Delaware	340.5	S,E	79.38	H	14.60[w]	34.91[w]	16.76 ± 2.44[w]	10.16 ± 12.93[w]	6.90×10^{-3}
Tenneco Chemicals, Inc.	Burlington, New Jersey	152.9	S,E	74.84	H,C	46.56[x]	11.75[x]	—[c,x]	—[c,x]	2.40×10^{-2}[e]
	Flemington, New Jersey	61.8	S,E	31.75	H,C	41.76[x]	10.20[x]	15.14 ± 9.78[x]	39.62 ± —[c,x]	9.60×10^{-3}
Union Carbide Corp.	South Charleston, West Virginia	95.4	S,E,B,SL	72.57	H,C	61.28[y]	5.24[y]	18.80 ± 3.41[y]	30.50 ± —[c,y]	2.09×10^{-2}
	Texas City, Texas	160.2	S,E,B,SL	136.08	H,C	48.23[z]	—[c,z]	21.34 ± 5.95[z]	21.34 ± 14.82[z]	2.39×10^{-2}
Uniroyal, Inc.	Painesville, Ohio	326.3	B,E	48.99	H	13.94[aa]	2.16[aa]	12.19 ± 2.71[aa]	17.47 ± 5.24[aa]	7.63×10^{-3}
Mean values (95% confidence limits)		312.9 ± 142		68.44 ± 11.61		35.45 ± 8.24	7.49 ± 3.18	15.49 ± 1.96	20.95 ± 3.41	$1.80 \times 10^{-2} \pm 5.27 \times 10^{-3}$

[a] S = Suspension, E = Emulsion, B = Bulk, SL = Solution, H = Homopolymer, and C = Copolymer.

[b] J. T. Barr, Air Products and Chemicals, Wayne, Pennsylvania, to Leslie B. Evans, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 24, 1974.

[c] Not available.

[d] N. J. Langer, American Chemical Corporation, Long Beach, California to Don R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 22, 1974.

[e] Average data substituted for not available data.

[f] W. B. Barton, Borden Inc., Columbus, Ohio to Don R. Goodwin (23, 26), July 1974.

[g] E. H. Smith, Continental Oil Co., Oklahoma City, Oklahoma to D. R. Goodwin, 12 July 1974.

[h] R. H. Gerlach, Continental Oil Co., Westlake, Louisiana to D. R. Goodwin, June 7, 1974.

[i] E. Eisn, Diamond Shamrock Chemical Company, Deer Park, Texas to L. B. Evans, February 24, 1975.

[j] W. C. Strader, Ethyl Corporation, Baton Rouge, Louisiana to D. R. Goodwin, April 22, 1975.

[k] F. F. Hoy, Firestone Plastics Company, Perryville, Maryland to D. R. Goodwin, June 7, 1974.

[l] C. J. Kleinert, Firestone Plastics Company, Pottstown, Pennsylvania to D. R. Goodwin, June 10, 1974.

[m] J. R. Mudd, The General Tire and Rubber Co., Ashtabula, Ohio to D. R. Goodwin, June 17, 1974.

[n] H. C. Holbrook, B. F. Goodrich Chemical Company, Cleveland, Ohio to D. R. Goodwin, June 17, 1974.

[o] D. J. Snyder, The Goodyear Tire and Rubber Co., Niagara Falls, New York to D. R. Goodwin, June 10, 1974.

[p] F. A. Cox, The Goodyear Tire and Rubber Co., Plaquemine, Louisiana to D. R. Goodwin, June 14, 1974.

[q] A. W. Fuhrman, Great American Chemical Corporation, Fitchburg, Massachusetts to D. R. Goodwin, June 1974.

[r] S. K. Law, Keysor-Century Corporation, Saugus, California to D. R. Goodwin, July 3, 1974.

[s] R. J. Abramowitz, Hooker Ruco Division, Burlington, New Jersey to D. R. Goodwin, June 20, 1974.

[t] R. E. Martel, Olin Chemicals, Assonet, Massachusetts to D. R. Goodwin, June 14, 1974.

[u] J. B. Hardwick, Pantasote Co., Passaic, New Jersey to D. R. Goodwin, June 14, 1974.

[v] H. E. Seyler, Robintech, Inc., Painesville, Ohio to D. R. Goodwin, June 14, 1974.

[w] G. Ford, Stauffer Chemical Company, Westport, Connecticut to D. R. Goodwin, June 10, 1974.

[x] W. P. Anderson, Tenneco Chemicals, Piscataway, New Jersey to D. R. Goodwin, June 11, 1974.

[y] R. N. Wheeler, Union Carbide Corp., South Charleston, West Virginia to D. R. Goodwin, June 6, 1974.

[z] M. E. Eisenhour, Union Carbide Corp., Texas City, Texas to D. R. Goodwin, June 27, 1974.

[aa] B. R. Leach, Uniroyal Chemical, Painesville, Ohio to D. R. Goodwin, June 13, 1974.

TABLE 14. SUMMARY OF CRITERIA USED TO DEFINE A REPRESENTATIVE POLYVINYL CHLORIDE PLANT

Criteria	Representative plant[a]
Process	Suspension process
Polymer	Homopolymer
Density, persons/km^2	310 ± 45%
Capacity, metric tons/yr	68,000 ± 17%
VCM emission factor, g/kg	36 ± 23%
PVC emission factor, g/kg	7.5 ± 42%
VCM emission height, m	16 ± 13%
PVC emission height, m	21 ± 16%
VCM ground level conc., g/m^3	0.018 ± 29%

[a]Numbers indicate the mean values; the 95% confidence limit is given as percent of the mean value.

TABLE 15. EMISSION FACTORS FOR A REPRESENTATIVE POLYVINYL CHLORIDE PLANT

Material emitted	Emission factor, g/kg
Vinyl chloride	35.5 ± 8.24[a]
Polyvinyl chloride	7.5 ± 3.18[a]
Stabilizer (phenol)	204 x 10^{-5}
Ethyl chloride	92 x 10^{-5}
Sulfur oxides	23 x 10^{-5}
Butadiene	21 x 10^{-5}
Hydrogen chloride	21 x 10^{-5}
Vinylidene chloride	9 x 10^{-5}
Acetaldehyde	7 x 10^{-5}
Acetylene	7 x 10^{-5}
Propylene	7 x 10^{-5}
Vinylacetylene	5 x 10^{-5}
Ethylene	5 x 10^{-5}
Ethylene dichloride	4 x 10^{-5}
Chloroprene	<4 x 10^{-5}
Vinyl bromide	2 x 10^{-5}

[a]Values indicate the mean values for the emission factor; the 95% confidence limit is given in g/kg.

TABLE 16. POLYVINYL CHLORIDE MANUFACTURING EMISSION FACTORS BY POINT OF EMISSION FOR A REPRESENTATIVE PLANT (g/kg)

Compounds emitted	Reactor safety relief valve	Reactor entry purge	Stripper jets	Monomer recovery condenser vent	Slurry blend tank vents	Centrifuge vents	Dryer discharge	Storage silos	Bulk Loading	Bagger vent	Storage tanks
Vinyl chloride	2.1[3]	2.8[a]	1.8[a]	5.0[3]	4.4[3]	1.3[a]	1.4[a]	0.7[3]	0[a]	0[a]	0.6[a]
Polyvinyl chloride	0[a]	0[a]	0[a]	0[a]	0[a]	1.3[3][a]	4.9[a]	0.7[3]	0.4[a]	0.2[a]	0[a]

	Transfer operations loading & unloading	Safety relief valve leaks and discharges	Pump, compressor & agitator seals	Sampling for laboratory analysis	Opening equipment for maintenance and inspection	Vacuum pumps and steam jets	Leaks at flanges, seals, etc.
Vinyl chloride	- - - - - - - - Total for all fugitive emissions sources is 15.3[1] - - - - - -						
Polyvinyl chloride	0	0	0	0	0	0	0

NOTE: Numerical superscripts (1) and (3) indicate reference numbers.

Superscript "a" indicates engineering estimate from information received from industry personnel (see footnotes concerning correspondence in Table 13).

Using the plant capacity and emission factor data shown in Tables 13 and 15, the emission rates shown in Table 17 were calculated. Using the emission heights for VCM emissions shown in Table 14 and Equations 1 and 2, values of χ_{max}, χ_{high} and χ_{low} were calculated as shown in Table 17. The mean values plus the 95% confidence limits for each value are shown at the bottom of the table.

Table 18 gives the time-averaged maximum ground level concentration by compound for a representative PVC plant. Table 19 gives the time-averaged maximum ground level concentration for each major point of emission.

Source Severity

To obtain a quantitative measure of the hazard potential of polyvinyl chloride manufacture, a source severity, S, is defined as the ratio of time-averaged maximum ground level concentration to F, the hazard exposure level for that pollutant; i.e., $S = \bar{\chi}_{max}/F$. F is the primary ambient air quality standard for criteria pollutants[a] and is a corrected threshold limit value (i.e., TLV • 8/24 • 1/100) for noncriteria pollutants.

Table 20 lists the source severity factor for each material emitted. Table 21 lists severity factors for each point of emission for the materials emitted. Table 22 contains the data (obtained from Table 18) used to prepare Figure 13, which shows the emission rate and the source severity for individual plants as a function of the cumulative percent of PVC plants. In Figure 13, TLV values for VCM were used to calculate source severity. Figure 14, which was developed from 1974 data, shows changes in plant emission rate and in plant source severity as a function of the cumulative percent of PVC plants. The primary ambient air quality standard for hydrocarbons was used to calculate the source severity of vinyl chloride. Figure 14 indicates that in 1974 the time-averaged maximum ground level concentrations of vinyl chloride emissions from all vinyl chloride plants exceeded the primary ambient air quality standard for hydrocarbons.

EPA conducted an ambient monitoring program around two plants which manufacture polyvinyl chloride. The facilities chosen were the Continental Oil Company's plant at Aberdeen, Mississippi, and the B. F. Goodrich Company's plant at Louisville, Kentucky (30).

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(30) EPA Programs of Monitoring Vinyl Chloride in Ambient Air. Environmental Protection Agency Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina, February 2, 1976. 14 pp.

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[a]Criteria pollutants are those emissions for which ambient air quality standards have been established.

TABLE 17. POLYVINYL CHLORIDE - SUMMARY OF PLANT DATA - II[a]

Plant location[b]	Q for VCM, g/s	χ_{max} (VCM), g/m^3	$\bar{\chi}_{max}$ (VCM), g/m^3	Vinyl chloride source severity
Calvert City, KY	72.5	6.26×10^{-3}	3.13×10^{-3}	360
Pensacola, FL	34.1	7.37×10^{-3}	3.68×10^{-3}	424
Long Beach, CA	10.2	2.22×10^{-3}[c]	1.11×10^{-3}	128
Illipolis, IL	51.7	8.92×10^{-3}	4.46×10^{-3}	513
Leominster, MA	66.7	1.46×10^{-2}[c]	7.28×10^{-3}	838
Springfield, MA	35.7[c]	7.79×10^{-3}[c]	3.90×10^{-3}	448
Aberdeen, MS	39.2[c]	8.56×10^{-3}[c]	4.28×10^{-3}	492
Oklahoma City, OK	11.6	2.53×10^{-2}[c]	1.27×10^{-2}	1,460
Delaware City, DE	51.0[c]	5.68×10^{-2}	2.84×10^{-2}	3,260
Deer Park, TX	13.2	2.28×10^{-3}	1.14×10^{-3}	131
Baton Rouge, LA	91.8[c]	2.00×10^{-2}[c]	1.00×10^{-2}	1,150
Perryville, MD	59.0	9.03×10^{-3}	4.51×10^{-3}	519
Pottstown, PA	132.0	2.87×10^{-2}[c]	1.44×10^{-2}	1,650
Ashtabula, OH	17.9	3.91×10^{-3}[c]	1.95×10^{-3}	225
Avon Lake, OH	171.0	2.87×10^{-2}	1.44×10^{-2}	1,650
Henry, IL	173.0	1.78×10^{-2}	8.91×10^{-3}	1,020
Long Beach, CA	48.0	2.00×10^{-2}	1.00×10^{-2}	1,150
Louisville, KY	161.0	5.74×10^{-2}	2.87×10^{-2}	3,300
Pedricktown, NJ	73.1	1.93×10^{-2}	9.63×10^{-3}	1,110
Niagara Falls, NY	57.5	2.51×10^{-2}	1.26×10^{-2}	1,450
Plaquemine, LA	122.0	2.39×10^{-2}	1.19×10^{-2}	1,370
Fitchburg, MA	6.3	1.38×10^{-3}[c]	6.88×10^{-4}	8
Saugus, CA	9.8	2.15×10^{-3}[c]	1.07×10^{-3}	123
Burlington, NJ	31.9	5.29×10^{-3}	2.64×10^{-3}	304
Hicksville, NY	7.6[c]	1.67×10^{-3}[c]	8.34×10^{-4}	10
Assonet, MA	76.5[c]	1.67×10^{-2}[c]	8.35×10^{-3}	961
Passaic, NJ	42.1	2.37×10^{-2}	1.18×10^{-2}	1,360
Point Pleasant, WV	113.0	5.76×10^{-2}	2.88×10^{-2}	3,310
Painesville, OH	126.0	3.63×10^{-2}	1.82×10^{-2}	2,090
Delaware City, DE	37.0	6.90×10^{-3}	3.45×10^{-3}	1,720
Burlington, NJ	110.0	2.40×10^{-2}[c]	1.20×10^{-2}	1,380
Flemington, NJ	42.0	9.60×10^{-3}	4.80×10^{-3}	552
South Charleston, WV	141.0	2.09×10^{-2}	1.05×10^{-2}	1,200
Texas City, TX	208.0	2.39×10^{-2}	1.20×10^{-2}	1,380
Painesville, OH	21.6	7.63×10^{-3}	3.82×10^{-3}	439
Mean values	70.43	1.80×10^{-2}	9.03×10^{-3}	1,071 ± 305
95% confidence limit	±18.86	$\pm 5.27 \times 10^{-3}$	$\pm 2.64 \times 10^{-3}$	

[a] Information extracted from specific sources corresponding to footnotes in Table 13.

[b] Plant locations correspond to those shown in Table 9.

[c] Average data not available.

TABLE 18. TIME-AVERAGED MAXIMUM GROUND LEVEL CONCENTRATION BY COMPOUND FOR A REPRESENTATIVE POLYVINYL CHLORIDE PLANT

Material emitted	Emission height, m	Q, g/s	χ_{max}, g/m^3	$\overline{\chi}_{max}$, g/m^3
Vinyl chloride	15.5 ± 1.96	76.9	1.7×10^{-2}	8.4×10^{-3}
Polyvinyl chloride	20.95 ± 3.41	16.2	1.9×10^{-3}	6.8×10^{-4}
Stabilizer (phenol)	15.5	4.4×10^{-3}	9.7×10^{-7}	4.8×10^{-7}
Ethyl chloride	15.5	2.0×10^{-3}	4.4×10^{-7}	2.2×10^{-7}
Sulfur oxides	15.5	5.0×10^{-4}	1.1×10^{-7}	5.4×10^{-8}
Butadiene	15.5	4.6×10^{-4}	9.9×10^{-8}	5.0×10^{-8}
Hydrogen chloride	15.5	4.6×10^{-4}	9.9×10^{-8}	5.0×10^{-8}
Vinylidene chloride	15.5	2.0×10^{-5}	4.3×10^{-8}	2.1×10^{-8}
Acetaldehyde	15.5	1.5×10^{-4}	3.3×10^{-8}	1.7×10^{-8}
Acetylene	15.5	1.5×10^{-4}	3.3×10^{-8}	1.7×10^{-8}
Propylene	15.5	1.5×10^{-4}	3.3×10^{-8}	1.7×10^{-8}
Vinylacetylene	15.5	1.1×10^{-4}	2.4×10^{-8}	1.2×10^{-8}
Ethylene	15.5	1.1×10^{-4}	2.4×10^{-8}	1.2×10^{-8}
Ethylene dichloride	15.5	8.7×10^{-5}	1.9×10^{-8}	9.5×10^{-9}
Chloroprene	15.5	8.7×10^{-5}	1.9×10^{-8}	9.5×10^{-9}
Vinyl bromide	15.5	4.3×10^{-5}	9.5×10^{-9}	4.7×10^{-9}

TABLE 19. TIME-AVERAGED MAXIMUM GROUND LEVEL CONCENTRATION FOR EMISSIONS FROM A REPRESENTATIVE POLYVINYL CHLORIDE PLANT BY POINT OF EMISSION

capacity = 68,440 metric tons/yr
emission height = 15.49 m for VCM and 20.95 m for PVC

Point of emission	Material emitted: Vinyl chloride Q, g/s	Vinyl chloride χ_{max}, g/m^3	Vinyl chloride $\overline{\chi}_{max}$, g/m^3	Polyvinyl chloride Q, g/s	Polyvinyl chloride χ_{max}, g/m^3	Polyvinyl chloride $\overline{\chi}_{max}$, g/m^3
Reactor safety relief valve	4.6	1.0×10^{-3}	4.5×10^{-4}	0	0	0
Reactor entry purge	6.1	1.3×10^{-3}	6.7×10^{-4}	0	0	0
Stripper jets	3.9	8.5×10^{-3}	4.3×10^{-4}	0	0	0
Monomer recovery condenser vents	10.8	2.4×10^{-3}	1.2×10^{-3}	0	0	0
Slurry blend tank vents	9.5	2.1×10^{-3}	1.1×10^{-3}	0	0	0
Centrifuge vents	2.8	6.2×10^{-4}	3.1×10^{-4}	2.8	3.3×10^{-4}	1.2×10^{-4}
Dryer discharge	3.0	6.6×10^{-4}	3.3×10^{-4}	10.6	1.3×10^{-3}	4.4×10^{-4}
Storage silos	1.5	3.3×10^{-4}	1.7×10^{-4}	1.5	1.8×10^{-4}	6.3×10^{-5}
Bulk loading	0	0	0	0.9	1.1×10^{-4}	3.8×10^{-5}
Bagger vents	0	0	0	0.4	4.8×10^{-5}	1.7×10^{-5}
Storage tanks	1.3	2.8×10^{-4}	1.4×10^{-4}	0	0	0
Fugitive emissions	33.2	7.3×10^{-3}	3.6×10^{-3}	0	0	0

TABLE 20. SOURCE SEVERITY BY COMPOUND FOR A REPRESENTATIVE POLYVINYL CHLORIDE PLANT

Material emitted	TLV, g/m^3	$\bar{X}_{max}$, g/m^3	F,[a] g/m^3	Source severity[b]
Vinyl chloride	0.0026	8.4×10^{-3}	8.7×10^{-6}	970
Polyvinyl chloride	0.1090	6.8×10^{-4}	3.6×10^{-4}	1.9
Stabilizer (phenol)	0.02	4.8×10^{-7}	6.7×10^{-5}	7.2×10^{-3}
Ethyl chloride	2.60	2.2×10^{-7}	8.7×10^{-3}	2.5×10^{-5}
Sulfur oxides	0.013	5.4×10^{-8}	4.3×10^{-5}	1.3×10^{-3}
Butadiene	2.20	5.0×10^{-8}	7.3×10^{-3}	6.8×10^{-6}
Hydrogen chloride	0.007	5.0×10^{-8}	2.3×10^{-5}	2.1×10^{-3}
Vinylidene chloride	0.004	2.1×10^{-8}	1.3×10^{-5}	1.6×10^{-3}
Acetaldehyde	0.18	1.7×10^{-8}	6.0×10^{-4}	2.8×10^{-5}
Acetylene	1.16	1.7×10^{-8}	3.9×10^{-3}	4.3×10^{-6}
Propylene	1.88	1.7×10^{-8}	6.3×10^{-3}	2.6×10^{-6}
Vinylacetylene	0.048	1.2×10^{-8}	1.6×10^{-4}	7.4×10^{-5}
Ethylene	1.25	1.2×10^{-8}	4.2×10^{-3}	2.8×10^{-6}
Ethylene dichloride	0.20	9.5×10^{-9}	6.7×10^{-4}	1.4×10^{-5}
Chloroprene	0.09	9.5×10^{-9}	3.0×10^{-4}	3.2×10^{-5}
Vinyl bromide	1.10	4.7×10^{-9}	3.7×10^{-3}	1.3×10^{-6}

[a] F = hazard factor = TLV • 8/24 • 1/100.

[b] $$\text{Source severity} = \frac{\bar{X}_{max}}{\text{TLV} \cdot 8/24 \cdot 1/100}$$

TABLE 21. SOURCE SEVERITY FOR A REPRESENTATIVE POLYVINYL CHLORIDE PLANT BY POINT OF EMISSION

Point of emission	Source severity for polyvinyl chloride emissions	Source severity for vinyl chloride emissions
Reactor safety relief valve	0	51.5
Reactor entry purge	0	76.7
Stripper jets	0	49.1
Monomer recovery condenser vent	0	136.0
Slurry blend tank vents	0	121.0
Centrifuge vents	0.32	35.5
Dryer discharge	1.22	37.7
Storage silos	0.17	19.2
Bulk loading	0.10	0
Bagger vent	0.05	0
Storage tanks	0	16.3
Fugitive emissions	0	417.0

TABLE 22. INPUT DATA

Vinyl chloride emission rate, 10^3 metric tons/yr	Cumulative percent of PVC plants	VCM source severity[a]	Hydrocarbon source severity[b]
0.10	2.9	8	0.43
0.20	5.7	10	0.54
0.24	8.6	123	6.7
0.31	11.4	128	6.9
0.32	14.3	131	7.1
0.42	17.1	225	12
0.56	20.0	304	16
0.68	22.9	360	20
1.08	25.7	424	23
1.13	28.6	439	24
1.16	31.4	448	24
1.33	34.3	492	27
1.33	37.1	513	28
1.51	40.0	519	28
1.61	42.9	552	30
1.63	45.7	838	45
1.81	48.6	961	52
1.86	51.4	1,020	55
2.10	54.3	1,110	60
2.29	57.1	1,150	62
2.31	60.0	1,150	62
2.41	62.9	1,200	65
2.89	65.7	1,360	74
3.49	68.6	1,370	74
3.58	71.4	1,380	75
3.66	74.3	1,380	75
3.86	77.1	1,450	79
3.98	80.0	1,460	79
4.15	82.9	1,650	89
4.18	85.7	1,650	89
4.45	88.6	1,720	93
5.09	91.4	2,090	113
5.39	94.3	3,260	177
5.46	97.1	3,300	179
6.56	100.0	3,310	199

[a] $S_{VCM} = \frac{\bar{\chi}_{max}}{TLV \cdot 8/24 \cdot 1/100}$

[b] $S_{hydrocarbon} = \frac{\bar{\chi}_{max}}{AAQS_{hydrocarbon}}$

where $AAQS_{hydrocarbon}$ = primary ambient quality standard for hydrocarbons.

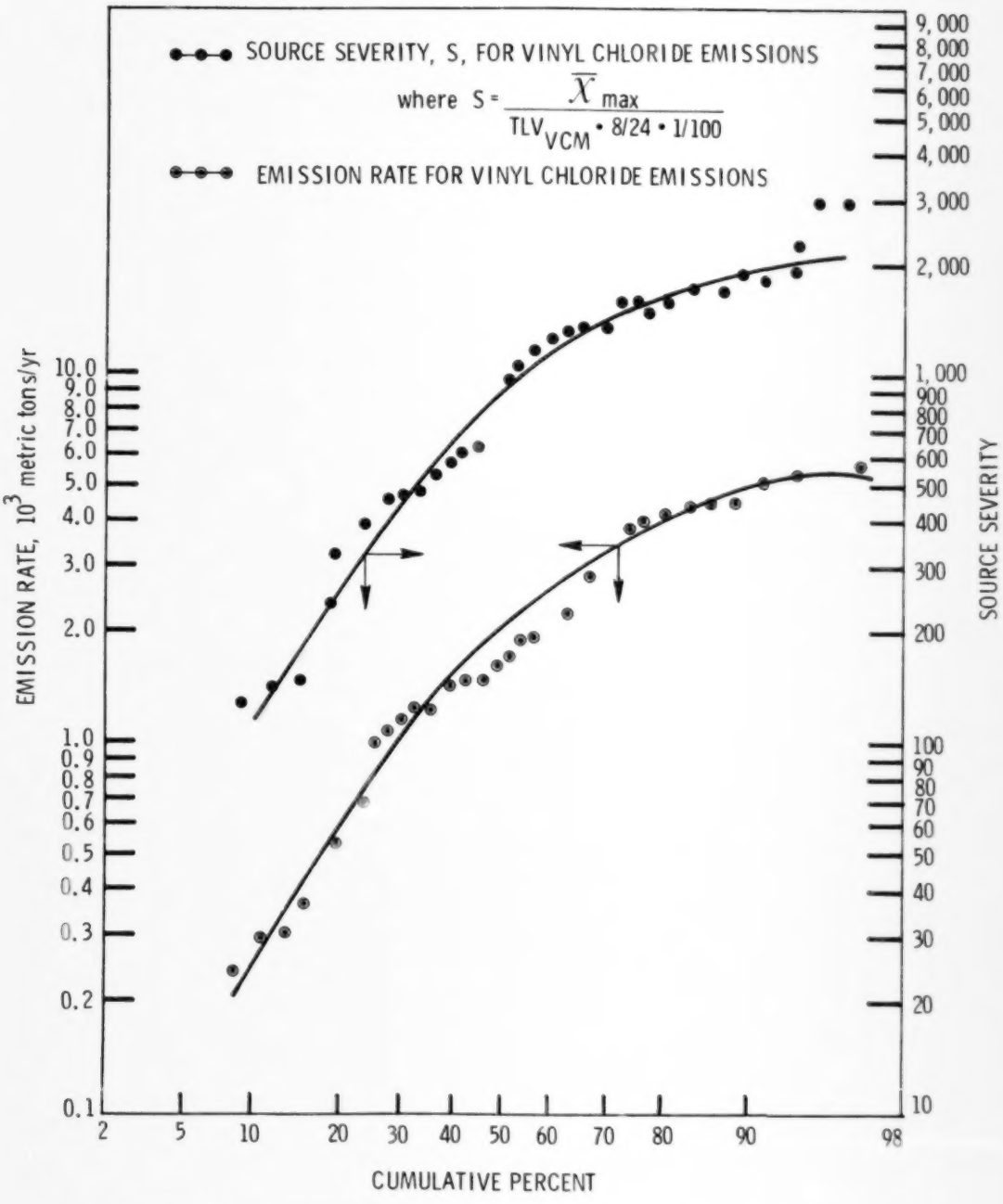

Figure 13. Cumulative percent of PVC plants having an emission rate and a source severity less than or equal to indicated value.

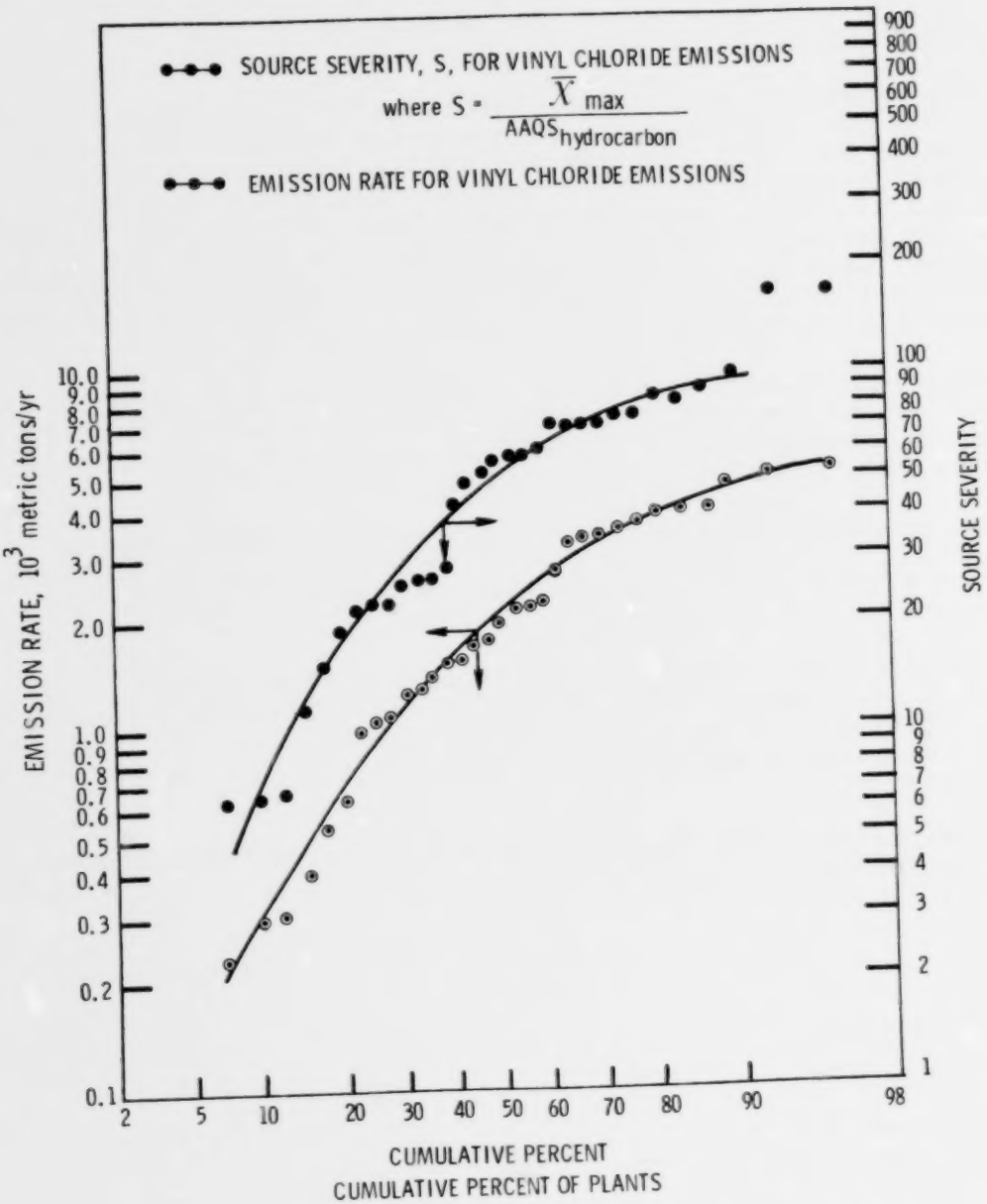
SOURCE SEVERITY, S, FOR VINYL CHLORIDE EMISSIONS
where S = $\frac{\overline{X}_{max}}{AAQS_{hydrocarbon}}$
EMISSION RATE FOR VINYL CHLORIDE EMISSIONS
EMISSION RATE, 10^3 metric tons/yr
SOURCE SEVERITY
CUMULATIVE PERCENT
CUMULATIVE PERCENT OF PLANTS

Figure 14. Cumulative percent of PVC plants having an emission rate and a source severity less than or equal to indicated value.

Integrated samplers were set up at various locations around the two plants. Each week two samples were collected at each sampling site and returned to the laboratory for gas chromatographic analysis (30).

At the Aberdeen, Mississippi plant, 15 24-hour integrated samplers were set up; 530 samples were collected between November 6, 1974, and March 27, 1975. At the Louisville, Kentucky plant, 17 24-hour integrated samplers were set up between November 6, 1974, and May 15, 1975. When it became clear that prevailing meteorological patterns were not as predicted, 38 24-hour integrated samplers were set up and a second set of samples collected between May 15, 1975, and June 12, 1975. A total of 1,155 samples were collected at the Louisville plant (30).

Information on wind direction and wind speed was recorded at each plant during the sampling effort. Also the plants recorded unusual occurrences which would be expected to affect their emission rates, and submitted these records to EPA (30).

Data obtained from the sampling program are summarized in Table 23. A histogram of the cumulative percent of samples having ground level concentration less than or equal to the indicated value is shown in Figure 15.

The ground level concentrations obtained from the sampling results are compared with the time averaged maximum ground level concentrations (from Table 17) calculated using the Gaussian plume dispersion methodology. These results are summarized in Table 24 (30).

$\bar{\chi}_{max}$ calculated for the 35 polyvinyl chloride manufacturing facilities using dispersion modeling ranged between 688 $\mu g/m^3$ and 28,800 $\mu g/m^3$; 30 plants have

$$976\ \mu g/m^3 < \bar{\chi}_{max} < 23{,}430\ \mu g/m^3,$$

3 plants have

$$\bar{\chi}_{max} > 23{,}430\ \mu g/m^3;$$

and 2 plants have

$$\bar{\chi}_{max} < 976\ \mu g/m^3.$$

TABLE 23. SUMMARY OF SAMPLING RESULTS (30)

Range of ground level concentrations, $\mu g/m^3$	Continental Oil Company Aberdeen, Mississippi			B. F. Goodrich Chemical Company Louisville, Kentucky		
	Number of observations	Percent of observations	Cumulative percent	Number of observations	Percent of observations	Cumulative percent
0 to 2	54	10.2	10.2	174	15.1	15.1
3 to 5	73	13.8	24.0	225	19.5	34.5
6 to 10	34	6.4	30.4	156	13.5	48.1
11 to 20	41	7.8	38.2	137	11.9	59.9
21 to 50	55	10.4	48.6	154	13.3	73.2
51 to 100	43	8.1	56.7	144	12.5	85.7
101 to 200	52	9.8	66.5	85	7.4	93.1
201 to 300	48	9.1	75.6	20	1.7	94.8
301 to 500	40	7.6	83.2	33	2.9	97.7
501 to 999	38	7.2	90.4	27	2.3	100.0
≥1,000	51	9.6	100.0	0	0.0	100.0
TOTAL	529	100.0	100.0	1,155	100.0	100.0
Maximum value found (24-hr avg)		23,430 $\mu g/m^3$			976 $\mu g/m^3$	

[a]Personal communication between S. R. Wyatt, EPA/SDB, Research Triangle Park, North Carolina and R. Turner, EPA/IERL, Cincinnati, Ohio, 9 June 1974.

TABLE 24. COMPARISON OF MEASURED AND CALCULATED EMISSION DATA

Continental Oil Company Aberdeen, Mississippi				B. F. Goodrich Chemical Company Louisville, Kentucky			
Calculated		Measured		Calculated		Measured	
$\bar{\chi}_{max}$, $\mu g/m^3$	Source severity	Maximum ground level concentration, $\mu g/m^3$	Source severity	$\bar{\chi}_{max}$, $\mu g/m^3$	Source severity	Maximum ground level concentration, $\mu g/m^3$	Source severity
4,280	492	23,430	2,690	28,700	3,300	976	112

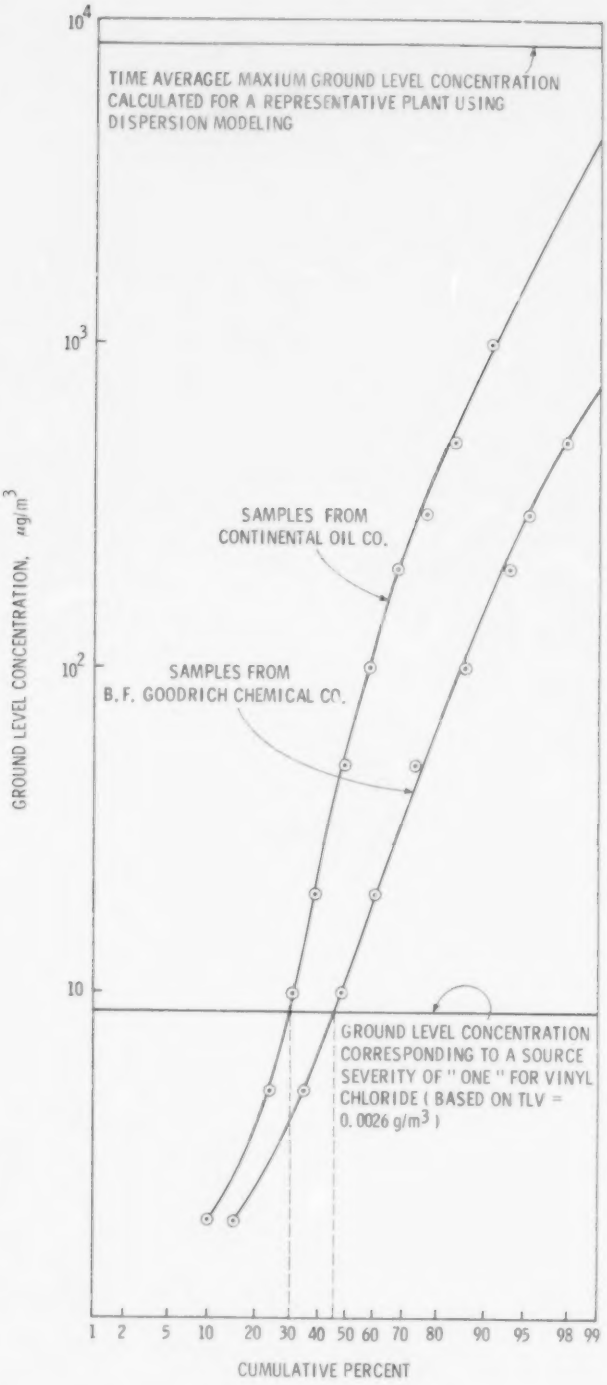
10^4
TIME AVERAGED MAXIUM GROUND LEVEL CONCENTRATION CALCULATED FOR A REPRESENTATIVE PLANT USING DISPERSION MODELING
10^3
SAMPLES FROM CONTINENTAL OIL CO.
10^2
SAMPLES FROM B.F. GOODRICH CHEMICAL CO.
10
GROUND LEVEL CONCENTRATION CORRESPONDING TO A SOURCE SEVERITY OF "ONE" FOR VINYL CHLORIDE (BASED ON TLV = 0.0026 g/m^3)
GROUND LEVEL CONCENTRATION, $\mu g/m^3$
1 2 5 10 20 30 40 50 60 70 80 90 95 98 99
CUMULATIVE PERCENT

Figure 15. Cumulative percent of samples having ground level concentrations less than or equal to indicated value.

From Figure 15 it is seen that 30% of the samples for the Aberdeen plant and 46% of the samples for the Louisville plant have ground level concentrations less than 8.7 $\mu g/m^3$ which corresponds to a source severity of "one" based on a TLV for vinyl chloride equal to 0.0026 g/m^3.

The EPA standard would result in a 95% or greater reduction in vinyl chloride emissions from polyvinyl chloride plants. Table 25 summarizes ambient ground level concentrations of controlled vinyl chloride emissions.

TABLE 25. CONTROLLED VINYL CHLORIDE EMISSIONS

	95% Controlled vinyl chloride emissions			
	Calculated		Measured	
Plant	$\bar{\chi}_{max}$, $\mu g/m^3$	Source severity (Basis: TLV = 0.0026 g/m^3)	$\bar{\chi}_{max}$, $\mu g/m^3$	Source severity (Basis: TLV = 0.0026 g/m^3)
Continental Oil Company	214	24.6	1,171.5	134.7
B. F. Goodrich Chemical Co.	1,435	165	48.8	5.6
Representative plant	420	48.3		

NOTE: Blanks indicate data not applicable.

Data used in the calculation of $\bar{\chi}_{max}$ was reported to EPA in early 1974. The sampling data was obtained in mid-1975. The glaring difference between measured and calculated ground level concentration for the B. F. Goodrich Chemical Company plant can be attributed in part to installation of control equipment during the crucial period when industry was involved in reducing emissions to comply with the temporary emission standard. Also at the time of sampling, the plant was operating at approximately 50 percent capacity.

All data used in this report were obtained prior to 1975. The polyvinyl chloride industry has undergone considerable modification since that time, and these results may not be currently representative.

Affected Population

The population affected by emissions from a typical PVC plant was obtained as described below.

The area exposed to the time-averaged ground level concentration, $\bar{\chi}$, for which $\bar{\chi}/F \geq 1.0$ was obtained by determining the area within the isopleth for $\bar{\chi}$ (31). The number of persons within the exposed area was then calculated, using the population density for a plant whose production and emission criteria closely match those used to define a representative plant. Table 26 shows the affected population for a representative PVC plant.

TABLE 26. AFFECTED AREA AND AFFECTED POPULATION

Parameter for representative plant	Particulates (polyvinyl chloride)	Hydrocarbon (vinyl chloride)
Population density, persons/km^2	313	313
Height of emission, m	21	15
TLV, g/m^3	0.11	0.003
Q, g/s	16	77
F (primary ambient air quality standard), g/m^3	3.6×10^{-4}	8.7×10^{-6}
χ_{max}, g/m^3	210	150
Maximum source severity	2.4	900
Affected area, A, km^2	11	2,800
Affected population, P, persons	3,400	870,000

GROWTH FACTOR

In 1974, 2.2×10^6 metric tons of polyvinyl chloride were produced in the United States; 1979 production is expected to total 2.62×10^6 metric tons. Vinyl chloride emissions from polyvinyl chloride manufacturing facilities have been estimated to be 35.5 g/kg of product as seen in Table 15. Therefore, total vinyl chloride emissions from polyvinyl chloride plants in 1974 are determined to have been 7.81×10^4 metric tons. The EPA requires vinyl chloride plants to reduce vinyl chloride emissions by 95%. Assuming proportional emission growth from 1974 through 1979, total 1979 vinyl chloride emissions to the atmosphere would be estimated as 9.26×10^4 metric tons. If all PVC manufacturing facilities reduce vinyl chloride emissions by 95%, total vinyl

(31) Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

chloride emissions to the atmosphere would be 4,640 metric tons. Therefore, vinyl chloride emissions from the polyvinyl chloride industry are expected to decrease by 94% from 1974-1979.

$$\frac{\text{Emissions in 1979}}{\text{Emissions in 1974}} = \frac{4{,}640 \text{ metric tons}}{78{,}100 \text{ metric tons}} = 0.06$$

SECTION 5

CONTROL TECHNOLOGY

Emissions from the manufacture of polyvinyl chloride consist of hydrocarbons and particulates. Table 27 shows the control equipment used for each emission point at a PVC plant.

CONTROL TECHNOLOGY FOR HYDROCARBONS

Activated Carbon Adsorption

Adsorption is a highly selective, three-step phenomenon in which molecules become attached to the surface of a solid. A given adsorbent or adsorbing agent will adsorb only certain types of materials, or adsorbates (32). First, the adsorbent comes in contact with the stream containing the adsorbate, and adsorption occurs. Next, the unadsorbed portion of the stream is separated from the adsorbent. Finally, removal of the adsorbate regenerates the adsorbent (33).

Activated carbon, the most suitable adsorbent for removing organic vapors (32), adsorbs 95% to 98% of all organic vapor from air at ambient temperature regardless of variations in concentration and humidity conditions (34).

When a gas stream is passed over an activated carbon bed, the carbon adsorbs the organic vapor or gas, and the purified stream passes through. Initially, adsorption is rapid and complete (32).

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(32) Air Pollution Engineering Manual, Second Edition. J. A. Danielson, ed. Publication No. AP-40, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1973. 987 pp.

(33) Hughes, T. W., D. A. Horn, C. W. Sandy and R. W. Serth. Source Assessment: Prioritization of Air Pollution from Industrial Surface Coating Operations. EPA-650/2-75-019-a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, February 1975. 303 pp.

(34) Hydrocarbon Pollutant Systems Study. Volume I. Stationary Sources, Effects and Control. APTD-1499 (PB 219 073), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 20, 1972. 379 pp.

TABLE 27. CONTROL TECHNOLOGY FOR POLYVINYL CHLORIDE MANUFACTURE (5)

Point of emission	Control equipment used[a]								
	Adsorption	Absorption	Refrigeration	Incineration	Stripping	Gasholder and water purge	Reactor entry purge control	Fugitive emission control	Particulate control
Reactor safety relief valve								∿50	
Reactor entry purge						X	X	∿50	
Stripper jets					50 to 80				
Monomer recovery condenser vent	50 to 99	50 to 90	40 to 60	50 to 99	50 to 80				
Slurry blend tank vent	50 to 99	50 to 90	40 to 60	50 to 99	50 to 80				
Centrifuge vent	50 to 99	50 to 90	40 to 60	50 to 99	50 to 80				X
Dryer discharge	50 to 99	50 to 90			50 to 80				X
Storage silos				50 to 99	50 to 80				X
Bulk loading								∿50	X
Bagger vent								∿50	X
Storage tank vents		50 to 90						∿50	
Fugitive emissions						X		∿50	

[a] Numbers indicate that range of control efficiency for control technology used, where X indicates that control technology is used at the emission point but its efficiency is not known.

NOTE: Blanks indicate not applicable.

As the carbon bed approaches its vapor-retaining capacity or breakpoint, traces of vapor appear in the exit air. If gas flow is continued, organic material is adsorbed, but at a decreasing rate.

The adsorption of a mixture of adsorbable organic vapors in air is not uniform. The more easily adsorbed components are those which have higher boiling points. When air containing a mixture of organic vapors passes over activated carbon, the vapors are equally adsorbed at the start. However, as the amount of the higher boiling constituents retained in the carbon bed increases, the more volatile vapors revaporize. After the breakpoint is reached, the exit vapor consists largely of the more volatile material (32). At this stage, the higher boiling component has displaced the lower boiling compound; the procedure is repeated for each additional component.

The quantity of an organic vapor adsorbed by activated carbon is a function of the nature of the vapor, the adsorbent type and temperature, and the vapor concentration. Removal of gaseous vapors by physical adsorption is practical for gases having molecular weights over 45 (35).

Each type of activated carbon has its own adsorbent properties for a given vapor. The quantity of vapor adsorbed for a particular vapor concentration and temperature is best determined experimentally. The quantity of vapor adsorbed increases when the vapor concentration increases and the adsorbent temperature decreases (33).

After reaching its breakpoint, the adsorbent is regenerated by heating the solids until the adsorbate is released. A carrier gas removes the vapors. Low pressure saturated steam is used as the heat source for activated carbon and also acts as the carrier gas. When high boiling compounds have reduced the carbon's adsorbing capacity to the point where complete regeneration is necessary, they may have to be removed with superheated steam at 350°C (33).

Steam requirements for regeneration are a function of external heat losses and the nature of the organic material. The amount of steam adsorbed per kilogram of adsorbate as a function of elapsed time passes through a minimum; the carbon should be regenerated for this length of time to permit the minimum use of steam (35). After regeneration, the carbon is hot and water-saturated. Organic-free air blown through the carbon bed evaporates the water and thus cools and dries the carbon. If high temperature steam has been used, other means of cooling the carbon are required.

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(35) Chemical Engineers Handbook, Fifth Edition. J. H. Perry and C. H. Chilton, eds. McGraw-Hill Book Company, New York, New York, 1973.

Fixed bed adsorbers arrayed in two or more parallel bed arrangements are used to remove organic vapors from air. These are batch-type arrangements, where a bed is used until breakthrough occurs and is then regenerated. The simplest adsorber design of this type is a two-bed system where one carbon bed is being regenerated as the other is adsorbing organic vapors. In a three-bed arrangement, a greater quantity of material can be adsorbed per unit of carbon because the effluent passes through two beds in series while the third bed is being regenerated. This permits the activated carbon to be used after breakthrough since the second bed in the series removes organic vapors in the exit gas from the first bed. When the first bed is saturated, it is removed from the stream for regeneration; the bed which was used to remove the final traces of organic vapors from the effluent then becomes the new first bed and the bed which has been regenerated becomes the new second bed (33).

Heat is released in the adsorption process, which causes the temperature of the adsorbent to increase. If the concentration of organic vapors is not high, as in the case of room ventilators, the temperature rise is typically 10°C (32, 33).

The pressure drop through a carbon bed is a function of the gas velocity, bed depth, and carbon particle size. Activated carbon manufacturers supply empirical correlations for pressure drop in terms of these quantities. These correlations usually include pressure drop resulting from directional change of the gas stream at the inlet and outlet (33).

Activated carbon systems are not economical when large volumes of gases containing low concentrations of organic compounds have to be treated. This technique for emission control has only recently been tried on high concentration streams in the PVC industry (4).

Carbon adsorption units are used to collect vinyl chloride from the monomer recovery system vent, centrifugal vent, and the slurry tank vent (4). The installation of carbon adsorption units at dryers and bulk storage silos depends on the life of the carbon bed.

Solvent Absorption

Absorption is a process for removing one or more soluble components from a gas mixture by dissolving them in a solvent.

Absorption equipment is designed to insure maximum contact between the gas and the liquid solvent, allowing interphase diffusion between the materials (32). Absorption rate is affected by factors such as the solubility of gas in the particular solvent and the degree of chemical reaction; however, the most important factor is the solvent surface exposed (32).

Equipment that disperses liquid solvent into the gas stream consists of packed towers, spray towers and venturi gas absorbers. Absorbers that use gas dispersion include tray towers and vessels with sparging equipment (32).

A packed tower is filled with one of many packing materials designed to expose a large surface area. When the solvent wets the packing surface, a large area of liquid film for contacting the solute gas is attained (32).

In spray-type absorbers, interphase contact is achieved by dispersing the liquid in a spray and passing the gas through it.

In venturi gas absorbers, interphase contact is provided through the different velocities of the gas and liquid, and by turbulence created in the venturi throat.

Tray towers induce contact by means of a number of trays arranged so that the gas is dispersed through a layer of solvent on each tray.

Solvents used to control vinyl chloride emissions include ethylene dichloride, acetone, "Carnea oil" (a petroleum based hydrocarbon), and trichloroethane (4).

The absorbed material, regenerated from the solvent by applying heat and vacuum, is then transferred to the monomer recovery system.

Solvent absorption units are installed to collect VCM from the monomer recovery condenser vent, storage area and slurry blend tank (4).

Refrigeration

Organic compounds can be removed from an air stream by condensation. A vapor will condense when, at a given temperature, the partial pressure of the compound is equal to or greater than its vapor pressure. Similarly, if the temperature of a gaseous mixture is reduced to the saturation temperature (i.e., the temperature at which the vapor pressure equals the partial pressure of one of the constituents), the material will condense. Thus, either increasing the system pressure or lowering the temperature can cause condensation (36).

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(36) Control Techniques for Hydrocarbons and Organic Solvent Emissions from Stationary Sources. Publication No. AP-68, U.S. Department of Health, Education, and Welfare, Washington, D.C., March 1970. pp. 3-1 through 3-26.

The equilibrium partial pressure limits the control of organic emissions by condensation. As condensation occurs, the partial pressure of material remaining in the gas decreases rapidly, preventing complete condensation. For example, at 0°C and atmosphere pressure, a gas stream saturated with toluene would still contain about 8,000 ppm of that gas. Thus a condenser is not very successful in reducing VCM emissions and must usually be followed by a secondary air pollution control device such as a carbon adsorber or solvent absorber (36).

Surface condensers are used in the PVC industry. VC vapor condenses on the outside surface of tubes while the cooling medium (water, freon, propane or propylene) flows within (4).

In the PVC plant, refrigeration is used on condenser vents, the slurry blend tank vent, and the centrifuge vent.

Incineration

On combustion, vinyl chloride forms hydrogen chloride, carbon dioxide and water:

$$2\ CH_2{=}CHCl + 5\ O_2 \rightarrow 4\ CO_2 + 2\ H_2O + 2\ HCl \qquad (3)$$

Little free chlorine should be formed since there is sufficient hydrogen in the VC molecule to combine with the chlorine and form hydrogen chloride. Chlorine inhibits oxidation reactions. Higher temperatures and longer residence times are needed for the complete destruction of pollutants if chlorine is present, even at low concentrations.

Table 27 identifies the emission points controlled by the types of incineration equipment described below.

Flares--
Flares are used for the combustion of low concentration vinyl chloride streams and intermittent emissions caused by plant upset (4). They are not an ideal form of control, because vinyl chloride oxidation produces hydrogen chloride which is itself a pollutant. Another disadvantage -- dilute gas streams cannot support combustion. Fuel must be added to achieve combustion, and the heat produced is wasted.

Direct-Flame Afterburners--
Direct-flame afterburners depend upon flame contact and high temperatures to burn combustible materials (37). The combustible

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(37) Rolkes, R. W., R. D. Hawthorne, C. R. Garbett, E. R. Slater, T. T. Phillips and G. D. Towell. Afterburner Systems Study. EPA-R2-72-062 (PB 212 560), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, August 1972. 512 pp.

materials may be gases, vapors, or entrained particulates which contribute opacity, odor, irritants, photochemical reactivity, and toxicity to the effluent. A direct-flame afterburner consists of a refractory-lined chamber, one or more burner temperature indicator-controllers, safety equipment, and, sometimes, heat recovery equipment (37).

The afterburner chamber consists of a mixing section and a combustion section. The mixing section provides contact between the contaminated gases and the burner flame. Good mixing is provided by high velocity flow which creates turbulence. The combustion section is designed to provide a retention time of 0.3 s to 0.5 s for completion of the combustion process. Afterburner discharge temperatures range from 540°C to 800°C, depending on the air pollution problem. Higher temperatures result in higher afterburner efficiencies (37).

The gas burners used in afterburners are of the nozzle-mixing, premixing, multiport, or mixing plate type. Burner placement varies depending on burner type and on the design objective of providing intimate contact of the contaminated air with the burner flames. When all the contaminated air passes through the burner, maximum afterburner efficiency is obtained (37).

Nozzle-mixing and premixing burners are arranged to fire tangentially into a cylindrical afterburner. Several burners or nozzles are required to ensure complete flame coverage, and additional burners or nozzles may be arranged to fire along the length of the burner. Air for fuel combustion is taken from the outside air or from the contaminated air stream which is introduced tangentially or along the major axis of the cylinder (37).

Multiport burners are installed across a section of the afterburner separate from the main chamber. Although all air for combustion is taken from the contaminated air stream, multiport burners are not capable of handling all of the contaminated air stream. Contaminated air in excess of that used for fuel combustion must be passed around the burner and mixed with the burner flames in a restricted and baffled area (37).

Mixing plate burners were developed for afterburner applications, and are placed across the inlet section of the afterburner. The contaminated air and the burner flames are mixed by profile plates installed around the burner between the burner and afterburner walls. The high velocities (1 m/s) provided by the burner and profile plate design ensure mixing of the burner flames and the contaminated air not flowing through the burner. The contaminated air stream provides air for fuel combustion (37).

The efficiency of an afterburner is a function of retention time, operating temperatures, flame contact, and gas velocity. No quantitative mathematical relationship between these variables exists because the kinetics of the combustion process are complex and flow inside afterburners is not defined. However, for good design, the following observations can be made with respect to afterburner efficiency (37).

- Efficiency increases with increasing after burner operating temperature.
- Efficiency decreases if the contaminated gases entering the afterburner are excessively preheated.
- Efficiency increases with increasing contact between the contaminated gases and the burner flame.
- Efficiency increases with increasing retention time for retention times less than 1 second.
- Efficiency is a function of the afterburner design and the inlet concentration of organic materials.
- Ninety percent afterburner efficiency is difficult to reach below a 700°C operating temperature if the generation of carbon monoxide in the afterburner is included.

Afterburners are designed to recover heat present in the combustion gases. When large volumes of dilute gases have to be burned, supplemental fuel is needed for combustion. Heat exchange can be used to reduce the amount of fuel required. Hot exit gases can also be used to generate steam in a boiler. The combustion gases leaving the heat exchanger or boiler may be scrubbed with water or caustic solution to remove hydrogen chloride.

Catalytic Afterburners--
A catalytic afterburner contains a preheat burner section, a chamber containing a catalyst, temperature indicators and controllers, safety equipment, and heat recovery equipment. The catalyst in such an afterburner promotes combustion by increasing the rate of the oxidation reactions without itself appearing to change chemically (33).

The contaminated air entering a catalytic afterburner is heated to the temperature necessary for carrying out the catalytic combustion. The preheat zone temperature, in the range of 340°C to 600°C, varies with the combustion and type of contaminants. Because of thermal incineration in the preheat zone, the preheat burner can contribute to the efficiency of a catalytic afterburner (33).

Catalysts used for catalytic afterburners may be platinum-family metals supported on metal or matrix elements made of ceramic honeycombs. Catalyst supports should have high geometric surface area, low pressure drop, structural integrity and durability, and should permit uniform distribution of the flow of the waste stream through the catalyst. Catalysts can be poisoned by phosphorus, bismuth, arsenic, antimony, mercury, lead, zinc, and tin, which are thought to form alloys with the metal catalyst. Catalysts are deactivated by materials which form coatings on them, such as particulate material, resins, and carbon formed during organic material breakdown. High temperatures will also deactivate catalysts. Because the combustion reaction is exothermic, the catalyst bed temperature is above the inlet temperature. The temperature increase depends on the concentration of organic material burned and the heat of combustion of that material. Compensation for decreased catalyst activity can be made by: 1) initial overdesign in specifying the quantity of catalyst required to attain required performance; 2) increasing preheat temperature as chemical activity decreases; 3) regenerating the catalyst; and 4) replacing the catalyst (33).

The quantity of catalyst required for 85% to 95% conversion of hydrocarbons ranges from 0.5 m^3 to 2 m^3 of catalyst per 1,000 m^3/min of waste stream. Although the catalyst temperature depends on the hydrocarbon burned and the condition of the catalyst, the operating temperature of catalytic afterburners ranges from 260°C to 540°C (37).

Steam Boilers--
Gaseous streams containing vinyl chloride can be incinerated in the fireboxes of steam boilers. Such a process requires appropriate instrumentation, however, because hydrogen chloride formed by combustion causes corrosion at temperatures above 316°C or below 204°C.

Concentrated hydrocarbon streams containing 1% to 18% vinyl chloride are used with supplemental natural gas and air to generate steam. The boiler is modified to burn chlorinated hydrocarbons. The exit of the boiler is scrubbed in a packed column with a wastewater stream having a pH of 11.

Slurry Stripping

After polymerization, unreacted VCM is removed from the reactor by venting. The vinyl chloride remaining in the water or trapped within PVC granules amounting to approximately 0.1% (38) must be effectively removed to control emissions from the slurry blend tank, the centrifuge, the dryer and the bulk storage silos (4).

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(38) Mantell, G. J., J. T. Barr and R. K. S. Chan. Vinyl Chloride Emission Control: Stripping VCM from PVC Resin. Chemical Engineering Progress 71(9):54-62, 1975.

The VCM remaining in the water or in the PVC granules is recovered by a process known as stripping, in which heat, pressure, and vacuum are used to drive off the volatile VCM from the reactor contents. The monomer so obtained is compressed and condensed for reuse (38).

The amount of VCM left after stripping depends on particle size and porosity, the temperature and vacuum used, and the retention time in the stripper. Increasing the temperature, reducing the pressure (i.e., increasing the vacuum) and increasing the duration of the stripping operation (residence) favor removal of the vinyl chloride from the resin (4).

Steam stripping involves increasing the temperature by introducing steam into the outside jacket of the reactor or into the vessel directly.

Countercurrent multistage column stripping is being investigated. The rate of VCM stripping is proportional to the difference between the amount of VCM in the resin and the amount of VCM in the water surrounding the resin. The primary advantage of countercurrent multistage column stripping is maximization of force because the resin leaving the column contacts water containing no vinyl chloride (4). Table 28 and Figure 16 show changes in monomer content, pressure, and temperature that occur when a batch of slurry is dropped from a reactor into the stripper. As seen from the figure, pressure increases rapidly, in the first few minutes followed by a slower fall to the operating pressure. The operating temperature is reached at the same time. This is defined as

TABLE 28. LOSSES OF MONOMER IN THREE STAGES OF STRIPPING OF BATCH FROM SLURRY OF 4,540 kg (10,000 lb) MONOMER CHARGE (38)

	Stages		
	I	II	III
VCM in resin, ppm:			
Initial	180,000	30,000	500
Final	30,000	500	1
Amount lost:[b]			
kg	580	114	1.8
lb	1,275	251	4

[a] Approximate conversion is 85%.

[b] Approximate weight ratios of monomer in vapor, liquid, and solid phases are 1:100:1000 during stripping.

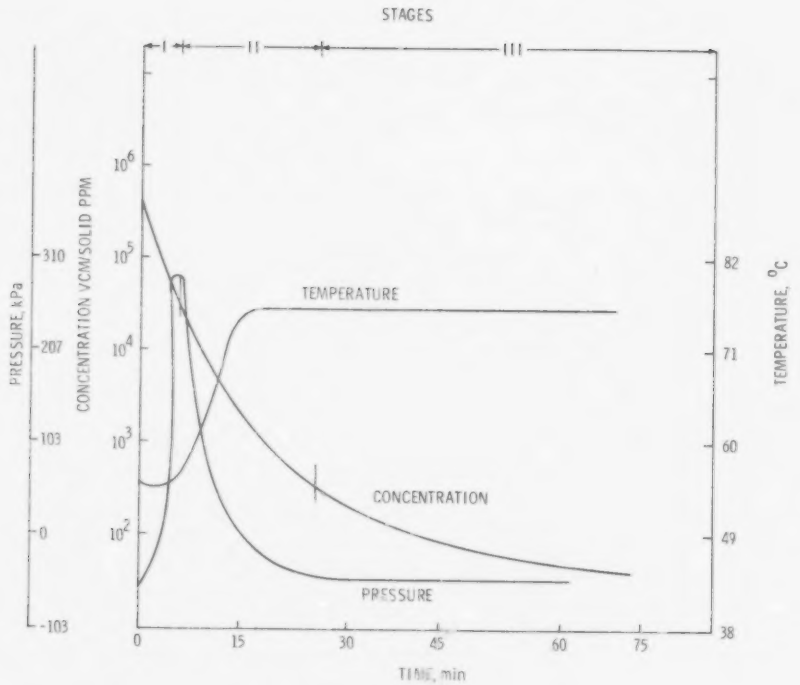

Figure 16. Stages of plant slurry stripping (38).

Stage I and generally results in an approximately 80% unreacted monomer reduction from approximately 18% in the solid to about 2% to 4%. In Stage II, the residual monomer drops to about 500 ppm. In Stage III where monomer residual is below 500 ppm and rates of VCM removal are at their lowest (38).

Product Stripping

Residual vinyl chloride retained by granular PVC can be removed in the storage silos by sweeping inert gas through the silos. The removal rate is low, but no major change in equipment is needed and the resin blending requirement is met (4). VCM recovered by the inert gas is removed by a carbon adsorber, solvent absorber, or incinerator. The inert gas can then be recycled back to the storage silos (4).

Gashol[illegible] Water Purge System

A gash[illegible]nd reactor water purge system can reduce emissions from [illegible]or entry purging, from reactor safety valve discharges, from [illegible]hloride recovery condenser vents, and from fugitive emissi[illegible]rces. Emissions are reduced by purging vinyl chloride fr[illegible]e reactor after the batch is discharged to the gashold[illegible]. Emissions from the recovery condenser vent are

reduced because there is less air left in the system before the reactor is charged (4). This increases the volume of gas that must be vented from the monomer recovery system.

The gasholder helps minimize reactor safety valve discharges. If upset conditions are noted, the reactor can be manually dumped to the gasholder which is sized to hold all of the VCM present in one batch.

The gasholder also acts as a surge tank between the plant and the vinyl chloride recovery system by holding a short-term, high volume surge of vinyl chloride which would normally overload the recovery system (4). The gasholder is also used to prevent fugitive emissions from other sources in the plant (4).

Reactor Entry Purge Control

Each time a reactor is opened for maintenance, cleaning or inspection, vinyl chloride emissions occur. These can be controlled by reducing the number of reactor openings. The use of high pressure water sprays inserted through a gland in the reactor to clean its walls reduces manual cleaning requirements to once every 12 batches.

The cleaning agent can be introduced as part of the reaction recipe, and reactors can be redesigned to minimize scale formation. These two procedures have reportedly reduced manual cleaning to once every 80 to 90 batches and in one case to one opening per 200 batches (4).

Heated organic solvent can be introduced into the reactor and agitated until the solid scales of PVC which line the reactor are broken up and dissolved. The mixture can then be distilled to separate the solvent, VCM and PVC. The solids are reclaimed or discarded, the monomer is recovered, and the solvent is recycled (4). In this case, the frequency of opening is reduced from once for each batch to once each 40 to 60 batches (4).

Control of Fugitive Emissions

Rapid detection and quick repair of a leak are necessary for reducing fugitive emissions. Leaks may be detected by several methods, and these are described below.

A fixed multipoint gas chromatograph, including analyzer and recorder, may be used to sample vinyl chloride periodically at points within the plant (4). The exact location of the leak in a section where a high concentration has been detected is determined by a portable flame ionization-type hydrocarbon sensing device (4).

Another method of detecting fugitive leaks is to periodically check each possible leak point with a portable detector (4). A third method is to hydrostatically test piping, flanges, vessels, manholes, and other process equipment after construction, maintenance, or inspection (4).

Control of pump, compressor, and agitator seals is provided by the use of double mechanical seals between which a liquid is maintained at a pressure greater than that which exists in the pump, compressor or agitator. Any leakage that occurs will thus leak into the pump, not out of it (4). All flanged pipe points are potential leak sources for which welded connections can be used.

Emissions resulting from sampling for laboratory analysis can be eliminated by letting the gas to be sampled flow through the sample flask to a lower pressure point in the process. The sample flask is then blocked off and any vinyl chloride that remains in the sample lines can be purged with inert gas to a monomer recovery system or a control device (4).

Two hoses are connected to a railroad car or barge for loading or unloading of VCM. The bottom hose transfers the liquid VCM while the other, located at the top, maintains pressure. Material left in the hoses may be lost to the atmosphere on disconnection. This can be controlled by purging the lines to a control device with inert gas (4).

Emissions resulting from excessive pressure are controlled by connecting the relief valve discharge to a flare or another control device. Vinyl chloride present in equipment that is opened for maintenance or inspection can be controlled by purging the equipment with inert gas or displacing the contents with water before opening (4).

CONTROL TECHNOLOGY FOR PARTICULATES

Fabric Filters

Fabric filters use a filter medium to separate particulate matter from a gas stream. Two types of fabric filters are in use: high energy cleaned collectors and low energy cleaned collectors (39).

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(39) Frey, R. E. Types of Fabric Filter Installations. Journal of the Air Pollution Control Association, 24(12):1148-1149, 1974.

High Energy Collectors--
In high energy collectors, pulse jets clean the filter medium, which is a felt fabric kept as clean as possible (39). The principle of the pulse jet is based on the use of an air ejector for dislodging dust from the bags. The ejector products a short pulse of compressed air in the direction opposite to that of the gas being filtered. The jet must accomplish three things (40): 1) stop normal filtering flow; 2) transmit a burst of air to the filtration medium to give it a vibratory shock; and 3) create enough pressure in the bag to assure a flow reversal from the clean side to the dirty side of the bag.

Low Energy Collectors--
Low energy collectors use shaking or reverse air flow methods of cleaning. The filter uses a woven cloth. However, the cloth itself is not the true filter medium, but rather acts as a site on which the true filter medium, dust cake, can build up (39).

Cyclones

In PVC production, cyclones are used to reduce the PVC dust emitted. Centrifugal and gravitational forces to the dust particles which are to be removed. This force is produced by directing the gas in a circular path or causing an abrupt change in direction. High density particles are forced against the wall of the cone in a spinning motion. The smaller the diameter of the cone, the faster the particles travel. Thus the particles become increasingly heavy through centrifugal force as they travel downwards in a spinning motion towards the bottom of the collector (32). Meanwhile the carrier gas spirals downward at the outside (with the dust particles) and upward at the inside of the cyclone, leaving the dust at the cone bottom.

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(40) Bakke, E. Optimizing Filter Parameters. Journal of the Air Pollution Control Association, 24(12):1150-1154, 1974.

SECTION 6

GROWTH AND NATURE OF THE INDUSTRY

PRESENT TECHNOLOGY

On January 22, 1974, the B. F. Goodrich Company notified NIOSH that four workers from its PVC polymerization plant in Louisville, Kentucky had died from a rare cancer, angiosarcoma (41). Since then the entire VCM and PVC industry has undergone considerable change as companies have tightened manufacturing processes to reduce exposures (42).

Worker exposure to VCM is being decreased by automating processes, reducing work forces, improving reactor cleaning methods (27), using larger reactors, improving stripping operations, and, in general, installing control equipment.

Polyvinyl chloride plants have reduced manual cleaning of reactors from once per batch to once every 12 batches (27). Between manual cleanings the reactor is cleaned with high pressure (68,950 kPa) water or solvent (27). The number of manual cleanings required can also be reduced by "clean wall" polymerization in which vessel walls are sprayed with a special material to prevent the polymer from sticking (27).

The use of large reactors is considered a major step forward in polyvinyl chloride technology (27). At present, 30% of the industry capacity is in reactors smaller than 10 m^3, and 70% of capacity is in reactors smaller than 20 m^3. Large reactors, with capacities over 70 m^3, will account for 16% to 20% of industry capacity by the end of 1975. Reactors with capacities up to 190 m^3 are currently in use. Larger reactors have fewer connections and therefore fewer potential leaks,

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(41) Preliminary Assessment of the Environmental Problems Associated with Vinyl Chloride and Polyvinyl Chloride. A Report on the Activities and Findings of the Vinyl Chloride Task Force. Compiled by the Office of Toxic Substances. Environmental Protection Agency, Washington, D.C. September 1974. 67 pp.

(42) Plastics Industry Developing Technology for VC Standard. Chemocology. Published by the Manufacturing Chemists Association, Washington, D.C., July 1975. p. 7.

and they require less manual cleaning. Entry for manual cleaning has been reduced by 90%, and only 25% of the personnel previously required are now needed for plant operation (27).

After polymerization, approximately 10% to 15% of the vinyl chloride monomer remains unreacted. Stripping is essential to control emissions from the slurry blend tank, centrifuge, dryer, and bulk storage silos (27). The effectiveness of stripping depends on the type of resin and the design of the stripping system. Other factors affecting stripping efficiency include particle size, porosity, temperature, vacuum used, and retention time in the stripper. Polyvinyl chloride manufacturers are phasing out grades of resin which are difficult to strip well. Stripping studies represent the area with the biggest potential payoff (27).

Currently available controls for VCM emissions are a basic part of the processing system and serves to recover reactant and product. These controls include: recycling of vent streams, condensation with refrigeration, adsorption to carbon, and absorption (scrubbing). Monomer loading and unloading involve special controls: vapor collection adapters with recycling, thermal level detectors with recycling, and magnetic gauges. Polymer controls include vacuum stripping, steam stripping, silos stripping, and recycling of carrier air streams (4).

EMERGING TECHNOLOGY

Vinyl chloride monomer and polymer manufacturing and processing industries have entered a new era since January 1974 when the link between vinyl chloride and cancer of the liver was noted and subsequently reported (43).

PVC manufacturing plants have controlled fugitive emissions by designing and installing new equipment to prevent leaks in the hundreds of pumps, valves and flanges used in their operations. As a result of these steps, VCM levels in PVC plants now average between 1 ppm and 3 ppm (44).

Polymerizer cleaning was a major emission source of VCM. Many companies have been involved in research to develop a completely closed, automated and essentially leak-proof system. One company reports using a "Clean Reactor Technology" which involves a combination of new processes, techniques and materials for treating the interiors of reactors. This system, plus others already

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(43) Researchers See Progress on VCM; Study New Hazards. Chemical Marketing Reporter. 207(13), 1975.

(44) Vercalin, C. H. Curtail Vinyl Chloride Exposure. Hydrocarbon Processing, 55(2):182, 184, 186, 1976.

developed, virtually elimijate the possibility of operator exposure to VCM in reactor cleaning and emptying operations (44).

Another source of VCM emissions is the VCM residual in PVC resins and compounds. The industry has developed new stripping columns which collect slurry from reactors and remove all but traces of the VCM remaining in the slurry.

The recovered VCM is cleaned in a closed system and recycled. The resulting resin contains less than 1 ppm of residual monomer, which may be further reduced in compounding or processing (44).

The stripping technology reduces the already low air and water emissions. Current reports indicate that VCM levels in outside air at the plant fence line are on the order of a few hundredths of a ppm. Further downwind from the plant, concentrations are further reduced by dilution with ambient air and also because of the actual breakdown of VCM molecules in the atmosphere (44).

INDUSTRY PRODUCTION TRENDS

In 1974, polyvinyl chloride homopolymer resins were produced by 20 companies at 35 plants. Four basic processes were used to produce the polymer: suspension, emulsion, bulk, and solution polymerization (4).

Suspension polymerization accounted for 78% of all PVC resin produced in the United States, while emulsion polymerization accounted for 13%. Bulk polymerization, a relatively new process, was used for 6% of the United States PVC production in 1974. Three percent of the resins produced in the United States were made by the solution polymerization process (2).

Production of polyvinyl chloride resins totaled 2.2×10^6 metric tons in 1974 (45). PVC production in the United States grew at an average rate of 14%/yr from 1963 to 1972 (3). In 1973, resin sales were 12% higher than the 1972 level and production was up 10% (46). After subtracting for exports, PVC sales in 1974 declined 3% from 1973 (45). OSHA regulations on the level of vinyl chloride emissions, the short supply of VCM, and the decrease in the supply of chlorine and plastizers have all been responsible for the decline in PVC sales (45).

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(45) Goodbye, Resin Storage? Don't You Believe It! Modern Plastics, 52(1):44-58, 1975.

(46) Now There's a Lot of Resin Around, But Economic Upturn Could Resume the Pinch. Modern Plastics, 51(12):18, 1974.

Figure 17 shows PVC production for the past 30 years. The shortage of resin supply in early 1974 created essentially a seller's market. By the end of 1974, there was a looseness in the resin market (46), even though supply had not changed, because of the recession of 1974-1975 (46). High interest rates, rising prices, inflation-deflated consumer spending power, and the slump in the automotive and housing industries were all responsible for the availability of PVC resins (46).

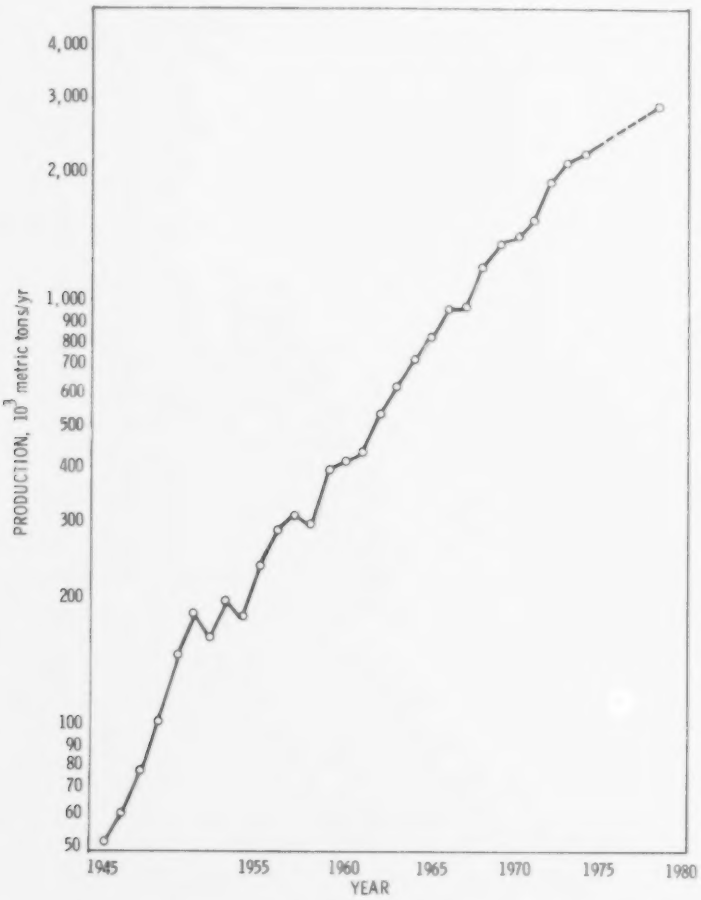

Figure 17. Polyvinyl chloride production, 1946-1979.

Table 29 summarizes U.S. consumption of polyvinyl chloride (47-52), and Figure 18 depicts this information graphically. Major PVC markets and their consumption of PVC resins over the past 3 years are shown in Table 30. Table 31 shows United States resin consumption by end use, and this is graphically illustrated in Figure 19.

TABLE 29. UNITED STATES CONSUMPTION OF POLYVINYL CHLORIDE RESIN BY COMPOUNDING PROCESS (10^3 metric tons)

Market	Year						
	1968 (47)	1969 (48)	1970 (49)	1971 (50)	1972 (51)	1973 (52)	1974 (45)
Calendering							
Flooring	111	127	113	131	156	133	92
Textile coating	NA[a]	NA	NA	29	32	33	39
Other (includes film and sheet)	238	272	259	218	283	249	263
Coating							
Flooring	26	30	34	52	58	69	64
Textile and paper coating	49	49	43	66	80	87	91
Protective coatings and adhesives	38	41	39	21	31	32	34
Other	NA	NA	NA	21	26	32	40
Extrusion							
Wire and cable	131	177	186	161	195	188	161
Film and sheet	61	68	82	92	103	93	98
Pipe and conduit	155	191	223	265	404	570	555
Other	NA	NA	NA	143	170	193	188
Molding							
Bottles	NA	NA	NA	33	32	39	34
Records	55	53	64	60	68	66	65
Pipe fittings	NA	NA	NA	34	39	41	44
Other	38	40	70	38	68	87	70
Paste processes							
Plastisol	49	57	52	47	50	39	39
Other	NA	NA	NA	23	28	32	35
Export	52	55	86	75	73	66	145
All other uses	77	88	102	72	79	102	123
TOTAL	1,080	1,247	1,371	1,571	1,975	2,151	2,180

[a]Not available.

(47) The Plastics Industry in 1968, Materials and Markets. Modern Plastics, 46(1):27-47, 1969.

(48) The Statistics: 1969. Modern Plastics, 47(1):69-80, 1970.

(49) The Statistics for 1970. Modern Plastics, 48(1):65-78, 1971.

(50) The Statistics for 1971. Modern Plastics, 49(1):41-48, 1972.

(51) Everything's Coming Up Roses, Thorns and All. Modern Plastics, 50(1):53-63, 1973.

(52) We Produced Over 13 Million Tons of Resins in '73? Well, Where Is It? And How About '74? Modern Plastics, 51(1):36-47, 1974.

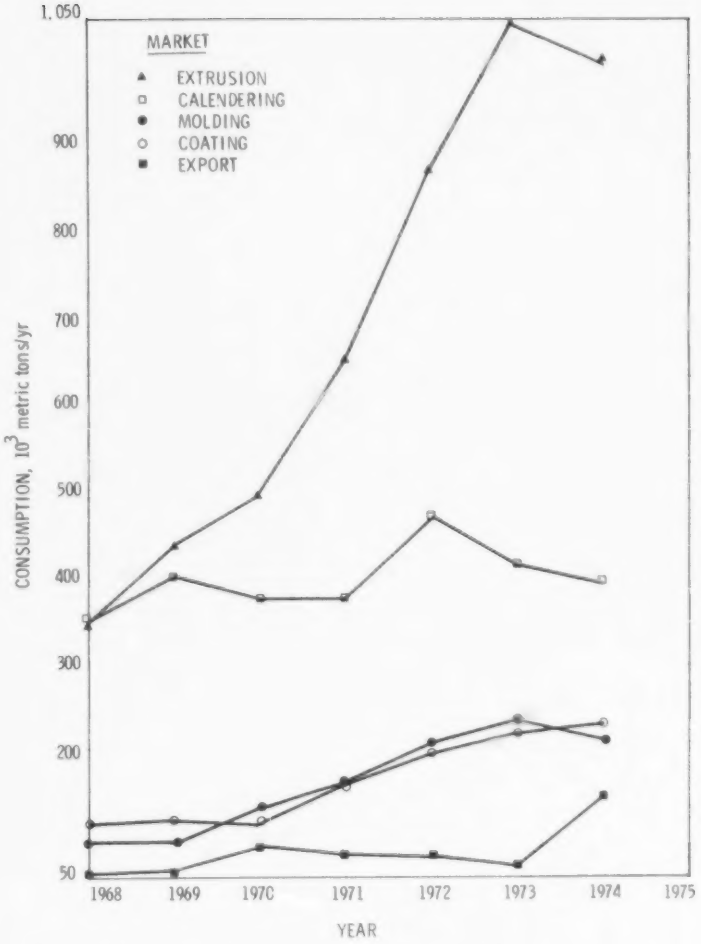

Figure 18. U.S. consumption of polyvinyl chloride by compounding process.

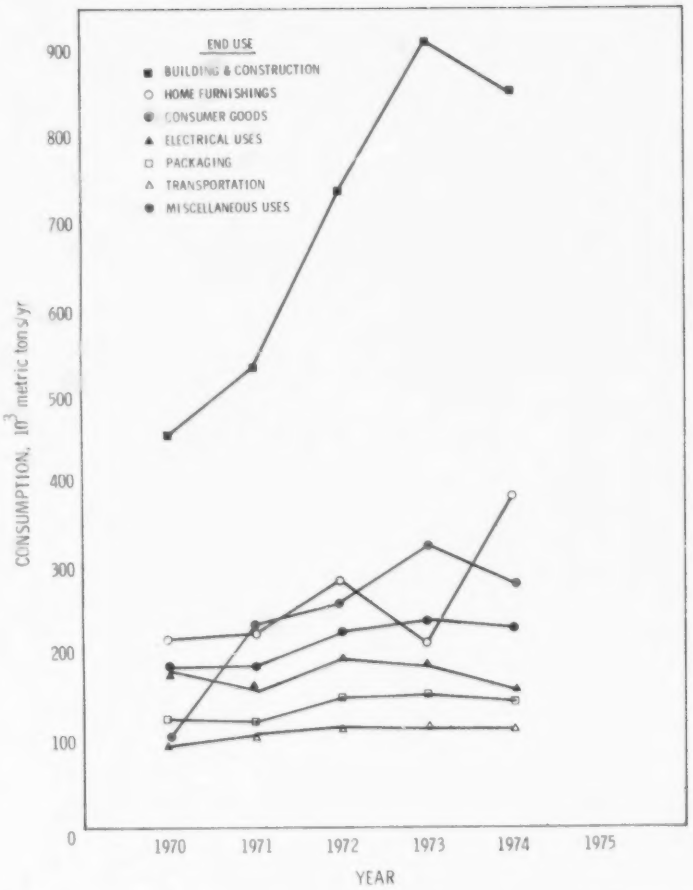

Figure 19. U.S. consumption of polyvinyl chloride by end use.

TABLE 30. CONSUMPTION OF POLYVINYL CHLORIDE BY MAJOR MARKETS (10^3 metric tons)

Market	1972 (51)	1973 (52)	1974 (45)
Apparel:			
Baby pants	11	12	11
Footwear	64	66	63
Outerwear	30	31	30
Building and construction:			
Extruded foam moldings	23	26	22
Flooring	214	202	156
Lighting	5	5	6
Panels and siding	32	39	44
Pipe and conduit	365	520	505
Pipe fittings	39	41	44
Rainwater systems, soffits, fascias	14	16	15
Swimming pool liners	20	18	19
Weatherstripping	18	16	16
Windows, other profiles	25	26	24
Electrical:			
Wire and cable	195	188	161
Home furnishings:			
Appliances	16	20	21
Furniture	135	145	144
Garden hose	20	18	17
Wall coverings and wood surfacing films	58	54	58
Packaging:			
Blow molded bottles	32	39	34
Closure liners and gaskets	8	9	10
Coatings	8	9	9
Film	62	59	57
Sheet	40	35	37
Recreation:			
Records	68	66	65
Sporting goods	23	25	28
Toys	34	38	37
Transportation:			
Auto mats	18	18	19
Auto tops	16	15	13
Upholstery and seat covers	82	83	84
Miscellaneous:			
Agriculture (including pipe)	53	66	72
Credit cards	7	8	10
Laminates	22	23	24
Medical tubing	21	23	23
Novelties	6	7	8
Stationery supplies	16	18	20
Tools and hardware	6	8	10
Export	73	66	145
Other	96	93	119
TOTAL	1,975	2,151	2,180

TABLE 31. UNITED STATES CONSUMPTION OF POLYVINYL CHLORIDE RESINS BY END USE
(10^3 metric tons)

End use catetory	1970 (49)	1971 (50)	1972 (51)	1973 (52)	1974 (45)
Building and construction	456	532	737	909	851
Home furnishing	219	225	286	219	384
Consumer good	188	188	229	238	234
Electrical uses	186	161	195	188	161
Packaging	123	122	150	151	147
Transportation	98	109	116	116	116
Miscellaneous uses and other unspecified uses	101	234	262	330	287
TOTAL	1,371	1,571	1,975	2,151	2,180

OUTLOOK

PVC resin consumption in the United States is expected to grow at an average rate of 8% between 1977 and 1981, leading to a consumption level of about 2.69×10^6 metric tons/yr by 1979 (53). Production expansion programs are cautious compared to recent years and could lag demand by 1981 according to current expectations. VCM expansions are seen as adequate (53).

Good growth is forseen for rigid extrusion products especially in the construction industry where pipe fittings and conduit already take one-third of production. Flooring, window components, and siding are being touted as areas open to extensive penetration by PVC. The automobile sector is expected to show moderate growth, due to shrinking cars (53).

Export markets will decline as Canadian production comes on stream, and world capacity increases faster than demand. Some smaller end uses, such as records, apparel and sporting goods, are not expected to show significant growth. Packaging has suffered since VCM was declared a carcinogen (53).

On the whole, the PVC industry has solved many of the technical and regulatory problems of recent years and can now look forward to good growth and increasing demand from many largest and use sectors (53).

(53) Chemical Profile: PVC. Chemical Marketing Reporter, 211(22):9, 35, 1977.

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APPENDIX

DERIVATION OF SOURCE SEVERITY EQUATIONS[a]

SUMMARY OF MAXIMUM SEVERITY EQUATIONS

The maximum severity of pollutants may be calculated using the mass emission rate, Q, the height of the emissions, H, and the ambient air quality standard, AAQS. The equations summarized in Table A-1 are developed in detail in this appendix.

TABLE A-1. POLLUTANT SEVERITY EQUATIONS FOR ELEVATED SOURCES

Pollutant	Severity equation
Particulate	$S_P = \frac{70\ Q}{H^2}$
Hydrocarbons	$S_{HC} = \frac{162\ Q}{H^2}$

DERIVATION OF χ_{max} FOR USE WITH U.S. AVERAGE CONDITIONS

The most widely accepted formula for predicting downwind ground level concentrations from a point source is (28):

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(A-1)}$$

where χ = downwind ground level concentration at reference coordinate x and y with emission height of H, g/m^3
Q = mass emission rate, g/s
σ_y = standard deviation of horizontal dispersion, m
σ_z = standard deviation of vertical dispersion, m
u = wind speed, m/s
y = horizontal distance from centerline of dispersion, m

[a]This appredix was prepared by T. R. Blackwood and E. C. Eimutis, Monsanto Research Corporation, Dayton Laboratory, Dayton, Ohio.

H = height of emission release, m
x = downwind emission dispersion distance from source of emission release, m
π = 3.14

We assume that χ_{max} occurs when x >>0 and y = 0. For a given stability class, standard deviations of horizontal and vertical dispersion have often been expressed as a function of downwind distance by power law relationships as follows (54):

$$\sigma_y = ax^b \tag{A-2}$$

$$\sigma_z = cx^d + f \tag{A-3}$$

Values for a, b, c, d, and f are given in Tables A-2 and A-3. Substituting these general equations into Equation A-1 yields:

$$\chi = \frac{Q}{ac\pi ux^{b+d} + a\pi ufx^b} \exp\left[-\frac{H^2}{2(cx^d + f)^2}\right] \tag{A-4}$$

Assuming that χ_{max} occurs at x <100 m or the stability class is C, then f = 0 and Equation A-4 becomes:

$$\chi = \frac{Q}{ac\pi ux^{b+d}} \exp\left[\frac{-H^2}{2c^2x^{2d}}\right] \tag{A-5}$$

For convenience, let:

$$A_R = \frac{Q}{ac\pi u} \text{ and } B_R = \frac{-H^2}{2c^2}$$

so that Equation A-5 reduces to:

$$\chi = A_R x^{-(b+d)} \exp\left[\frac{B_R}{x^{2d}}\right] \tag{A-6}$$

Taking the first derivative of Equation A-6

$$\frac{d\chi}{dx} = A_R \left\{ x^{-b-d}\left[\exp\left(B_R x^{-2d}\right)\right]\left(-2dB_R x^{-2d-1}\right) + \exp\left(B_R x^{-2d}\right)\left(-b-d\right)x^{-b-d-1}\right\} \tag{A-7}$$

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(54) Martin, D. O., and J. A. Tikvart. A General Atmospheric Diffusion Model for Estimating the Effects on Air Quality of One or More Sources. Presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minnesota, June 23-27, 1968. 18 pp.

TABLE A-2. VALUES OF a FOR THE COMPUTATION OF σ_y[a] (54)

Stability class	a
A	0.3658
B	0.2751
C	0.2089
D	0.1471
E	0.1046
F	0.0722

[a]For Equation A-2: $\sigma_y = ax^b$

where x = downwind distance
b = 0.9031 (Reference 55)

TABLE A-3. VALUES OF THE CONSTANTS USED TO ESTIMATE VERTICAL DISPERSION[a] (54)

Usable range, m	Stability class	Coefficient		
		c_1	d_1	f_1
>1,000	A	0.00024	2.094	-9.6
	B	0.055	1.098	2.0
	C	0.113	0.911	0.0
	D	1.26	0.516	-13
	E	6.73	0.305	-34
	F	18.05	0.18	-48.6
		c_2	d_2	f_2
100 to 1,000	A	0.0015	1.941	9.27
	B	0.028	1.149	3.3
	C	0.113	0.911	0.0
	D	0.222	0.725	-1.7
	E	0.211	0.678	-1.3
	F	0.086	0.74	-0.35
		c_3	d_3	f_3
<100	A	0.192	0.936	0
	B	0.156	0.922	0
	C	0.116	0.905	0
	D	0.079	0.881	0
	E	0.063	0.871	0
	F	0.053	0.814	0

[a]For Equation A-3: $\sigma_z = cx^d + f$

(55) Eimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6(11): 859-863, 1972.

and setting this equal to zero (to determine the roots which give the minimum and maximum conditions of χ with respect to x) yields:

$$\frac{d\chi}{dx} = 0 = A_R x^{-b-d-1}\left(\exp\left[B_r x^{-2d}\right]\right)\left(-2dB_r x^{-2d} - b - d\right) \qquad \text{(A-8)}$$

Since we define that $x \neq 0$ or ∞ at χ_{max}, the following expression must be equal to 0:

$$-2dB_r x^{-2d} - d - b = 0 \qquad \text{(A-9)}$$

Therefore

$$(b + d)\ x^{2d} = -2dB_R \qquad \text{(A-10)}$$

or

$$x^{2d} = \frac{-2dB_R}{b + d} = \frac{2d\ H^2}{2c^2(b + d)} = \frac{d\ H^2}{c^2(b + d)} \qquad \text{(A-11)}$$

Hence

$$x = \left(\frac{d\ H^2}{c^2(b + d)}\right)^{\frac{1}{2}d} \text{ at } \chi_{max} \qquad \text{(A-12)}$$

Thus Equations A-2 and A-3 (at f = 0) become:

$$\sigma_y = a\left(\frac{d\ H^2}{c^2(d + b)}\right)^{b/2d} \qquad \text{(A-13)}$$

$$\sigma_z = c\left(\frac{d\ H^2}{c^2(b + d)}\right)^{d/2d} = \left(\frac{d\ H^2}{b + d}\right)^{\frac{1}{2}} \qquad \text{(A-14)}$$

The maximum will be determined for U.S. average conditions of stability. According to Gifford (56), this is when $\sigma_y = \sigma_z$. Since b = 0.9031, and upon inspection of Table A-2 under U.S.

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(56) Gifford, F. A., Jr. An Outline of Theories of Diffusion in the Lower Layers of the Atmosphere. In: Meteorology and Atomic Energy 1968, Chapter 3, D. A. Slade, ed. Publication No. TID-24190, U.S. Atomic Energy Commission Technical Information Center, Oak Ridge, Tennessee, July 1968. p. 113.

average conditions, $\sigma_y = \sigma_z$, it can be seen that $0.881 \leq d \leq 0.905$ (class C stability[a]). Thus, it can be assumed that b is nearly equal to d in Equations A-13 and A-14 or:

$$\sigma_z = \frac{H}{\sqrt{2}} \tag{A-15}$$

and

$$\sigma_y = \frac{a}{c} \frac{H}{\sqrt{2}} \tag{A-16}$$

Under U.S. average conditions, $\sigma_y = \sigma_z$ and a = c if b = d and f = 0 (between class C and D, but closer to belonging in class C).

Then

$$\sigma_y = \frac{H}{\sqrt{2}} \tag{A-17}$$

Substituting for σ_y from Equation A-17 and for σ_z from Equation A-15 into Equation A-1 and letting y = 0:

$$\chi_{max} = \frac{2\,Q}{\pi u H^2} \exp\left[-\frac{1}{2}\left(\frac{H\sqrt{2}}{H}\right)^2\right] \tag{A-18}$$

or

$$\chi_{max} = \frac{2\,Q}{\pi e u H^2} \tag{A-19}$$

DEVELOPMENT OF SOURCE SEVERITY EQUATIONS

Source severity, S, has been defined as follows:

$$S = \frac{\overline{\chi}_{max}}{AAQS} \tag{A-20}$$

where $\overline{\chi}_{max}$ = time-averaged maximum ground level concentration
AAQS = ambient air quality standard

[a]The values given in Table A-3 are mean values for stability class. Class C stability describes these coefficients and exponents, only within about a factor of two.

Values of $\bar{\chi}_{max}$ are found from the following equation:

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{t_o}{t}\right)^{0.17} \qquad \text{(A-21)}$$

where t_o is the "instantaneous" (i.e., 3-min) averaging time and t is the averaging time used for the ambient air quality standard as shown in Table A-4.

TABLE A-4. SUMMARY OF NATIONAL AMBIENT AIR QUALITY STANDARDS (57)

Pollutant	Averaging time	Primary standards	Secondary standards
Particulate	Annual (geometric mean)	75 $\mu g/m^3$	60[a] $\mu g/m^3$
	24 hr[b]	260 $\mu g/m^3$	150 $\mu g/m^3$
Hydrocarbons (nonmethane)	3 hr (6 to 9 a.m.)	160 $\mu g/m^3$ (0.24 ppm)	(Same as primary)

[a]The secondary annual standard (60 $\mu g/m^3$) is a guide for assessing implementation plans to achieve the 24-hr secondary standard.

[b]Not to be exceeded more than once per year.

Hydrocarbon Severity

The primary standard for hydrocarbon is reported for a 3-hr averaging time. Therefore, t = 180 min. Hence, from Equation A-21:

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{3}{180}\right)^{0.17} = 0.5\chi_{max} \qquad \text{(A-22)}$$

Substituting for χ_{max} from Equation A-19 yields:

$$\bar{\chi}_{max} = \frac{(0.5)(0.052)\ Q}{H^2} = \frac{0.026\ Q}{H^2} \qquad \text{(A-23)}$$

For hydrocarbons, AAQS = 1.6×10^{-4} g/m^3. Therefore

$$S = \frac{\bar{\chi}_{max}}{AAQS} = \frac{0.026\ Q}{1.6 \times 10^{-4}\ H^2} \qquad \text{(A-24)}$$

(57) Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 - National Privacy and Secondary Ambient Air Quality Standards, April 28, 1971. 16 pp.

or

$$S_{HC} = \frac{162.5\ Q}{H^2} \qquad \text{(A-25)}$$

Particulate Severity

The primary standard for particulate is reported for a 24-hr averaging time. Therefore, t = 1,440 minutes. Hence, for Equation A-21:

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{3}{1,440}\right)^{0.17} \qquad \text{(A-26)}$$

Substituting for χ_{max} from Equation A-19 yields:

$$\bar{\chi}_{max} = \frac{0.052\ Q}{H^2}\ (0.35) = \frac{0.0182\ Q}{H^2} \qquad \text{(A-27)}$$

For particulates, AAQS = 2.6×10^{-4} g/m^3. Therefore

$$S = \frac{\bar{\chi}_{max}}{AAQS} = \frac{0.0182\ Q}{2.6 \times 10^{-4}\ H^2} \qquad \text{(A-28)}$$

or

$$S_P = \frac{70\ Q}{H^2} \qquad \text{(A-29)}$$

AFFECTED POPULATION CALCULATION

Another form of the plume dispersion equation is needed to calculate the affected population since the population is assumed to be distributed uniformly around the source. If the wind directions are taken to 16 points and it is assumed that the wind directions within each sector are distributed randomly over a period of a month or a season, it can be assumed that the effluent is uniformly distributed in the horizontal within the sector. The appropriate equation for average concentration, $\bar{\chi}$, in g/m^3 is then (57):

$$\bar{\chi} = \frac{2.03\ Q}{\sigma_z ux} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(A-30)}$$

To find the distances at which $\bar{\chi}$/AAQS = 1.0, roots are determined for the following equation:

$$\frac{2.03\ Q}{(AAQS)\ \sigma_z ux} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] = 1.0 \qquad \text{(A-31)}$$

keeping in mind that:

$$\sigma_z = ax^b + c$$

where a, b, and c are functions of atmospheric stability and are assumed to be selected for stability Class C. Since Equation A-28 is a transcendental equation, the roots are found by an iterative technique using the computer.

For a specified emission from a typical source, $\bar{\chi}$/AAQS as a function of distance might look as follows:

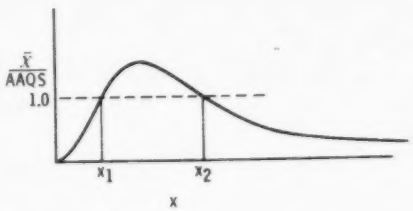

Figure A-1. $\frac{\bar{\chi}}{AAQS}$ as a function of distance from source.

The affected population is contained in the area

$$A = \pi(x_2^2 - x_1^2) \qquad \text{(A-32)}$$

If the affected population density is D_p, the total affected population, P, is

$$P = D_p A \text{ (persons)} \qquad \text{(A-33)}$$